Assessing the controls of the fluoride concentrations in the groundwater of Gothenburg area

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Abstract

The human uptake of fluoride can promote healthy teeth in low concentration (<1.5 mg/l) or cause fluorosis when concentration is high (>1.5 mg/l). Drinking water is a major route to which we humans are expose to fluoride intake. The work presented in this thesis was carried out along the west coast of the Gothenburg area exploring the sources of fluoride in groundwater, the controls the fluoride groundwater concentration and its risks for human health. To this end, we used the water analysis from 2537 private wells and evaluated the relation of their fluoride content to the geological units. Higher concentrations of fluoride in groundwater were related to basement rocks especially granitic rocks, whereas the dissolution of the fluoride-bearing biotite, hornblende, and fluorite were mainly responsible for the fluoride accumulation in groundwater. The concentration of fluoride in the collected samples ranged between *0 mg/l* to *16 mg/l* with most of the samples ranging mainly between *0 - 8.9 mg/l* with a small number of samples ranging between *10 - 16 mg/l*. At least 17% of the household were at risk of mild to severe fluorosis upon consumption of water that contain fluoride concentration higher than the 1.5mg/l limit. A high number of private wells located in the Bohus granite showed to contain high fluoride concentration. This high fluoride concentration was shown to be associated with high radioactive measurements of uranium and thorium because of their late crystallisation during the magma fractionating process. Moreover, calculations of saturation indices for fluoride-bearing minerals using PHREEQC revealed that fluorite was the only mineral at or close to saturation. This showed that the maximal fluoride concentration in groundwater in the Gothenburg area is likely solubility controlled by the mineral fluorite in all different rock units.

Keywords: Fluoride, Groundwater, Fluorite, Solubility, fluorosis, Idefjorden Terrane.

I. Introduction

Access to clean drinking water is very important for human health. The most important source of drinking water is groundwater since it makes up about 99% of the available global freshwater resources (Carrard et al, 2019). As such there is the need to protect groundwater and to make it safe for consumption. In the United Nations, 2018 edition of their sustainable development goals for 2030, the sixth goal highlights the need for clean water to be available for everyone and that it be used in a sustainable manner. One of the geogenically dissolved species in groundwater that has a negative health impact on millions of humans is fluoride if it is present in concentrations higher than 1.5 mg/l (WHO, 2008). The ionic form of the element fluorine is called fluoride and belongs to the halogen group. Fluorine is the 13th most abundant element in nature and the most reactive and electronegative element (Martinez-Mier, 2011; T. Berger, 2016). The element fluorine is abundant in silicate minerals as it is formed late in the magmatic crystallization process (T. Berger, 2016). Fluorine is found in naturals waters as dissolved fluoride, F^-. According to Anuradha and Jagvir (2021) and Berger (2016), 60% of fluoride intake by humans occurs through drinking water. The remaining 40% comes from food, air, medicine, and cosmetics. Fluoride is a tasteless, odourless, and colourless substance and when present in water one cannot easily tell whether the water contains high or low concentrations of fluoride (WHO, 2001)

The WHO (2008) has set permissible limits for the fluoride concentrations in groundwater that is used for drinking water purposes to 1.5 mg/l. Tab. 1 below outlines fluoride concentrations and their corresponding health effects. Hence, when the amount of fluoride in drinking water is high, it calls for concern as high intake of fluoride can cause dental, skeletal, and non-skeletal forms of fluorosis (Sahu et al, 2020). Skeletal fluorosis occurs when a lot of fluoride accumulates in the bones and joints of the human body through respiration or ingestion over a long period of time. The concentrations of these high amounts of fluoride in the bones and joints will cause bone resorption and alter the levels of calcium in bone tissue. The common symptoms here are chronic joint pain, joint stiffness, calcification of ligament and osteosclerosis (Sandra E. J. and Abraham J., 2016). Disturbance of the normal development of the enamel is called dental fluorosis. During the calcification of the teeth of children (aged 0-12 years), the exposure to high amounts of fluoride will cause the dental enamel to start mottling. Upon prolonged intake of this high amounts of fluoride, the enamel of the teeth will become hard and brittle. Fluorine poses one the greatest health challenges (WHO, 2008; 2011). In areas where there is little or no infrastructure to control the negative impacts caused by high

fluoride concentration, there have been widespread cases of fluorosis (Berger, 2012). Since as drinking water is a primary source for fluoride intake by humans, there is a need to monitor the public drinking water systems. Many studies have been carried out on the negative impact of high fluoride concentration in humans based only on the influence of drinking water while others have suggested a combination of several sources such as drinking water, food beverages, dental products, and soil particles (T. Berger, 2014). The sources of fluoride in groundwater could either be from the soil or rock they pass through.

Despite having adverse health effects at high concentrations, fluoride has health benefits in drinking water if the concentration does not exceed the permissible limit of 1.5 mg/l (WHO, 2006; S. M. Mazhar et al, 2013). This acceptable fluoride limit in drinking water is the same as the European Drinking Water Directive (98/83/EC) and in Sweden legislation. A health benefit of fluoride includes the strengthening of teeth enamel since fluoride can replace the OH of hydroxyapatite ($Ca_5(PO_4)_3(OH)$) to form fluorapatite ($Ca_5(PO_4)_3(F)$) in the teeth enamel which is more resistant against tooth decay than hydroxyapatite (A. Ayoob and K. Gupta, 2006; Yani et al, 2019).

Table 1: Health effects of fluoride concentration in drinking water (modified from Dissanayake 1991)

Fluoride Concentration (mg/l)	**Chronic health effects**
0.5 - 1.5	Promotes dental health, prevents tooth decay
1.5 - 4	Dental fluorosis (mottled teeth)
4 - 10	Dental fluorosis, skeletal fluorosis
>10	Crippling fluorosis

Situation in Sweden

In Sweden, high fluoride groundwater concentrations are also occurring which can cause health problems. In Sweden, water for public consumption is regulated and monitored in line with the Swedish Food Agency (Livsmedelsverket, 2001).

According to the report of Statistics Sweden 2015, household water consumption is provided either by the municipalities or through approximately 500,000 private wells. The municipality waterworks is supplied to around 88% of the population while private wells account for about 12%. Water provided by the municipality comes from two sources: 1/3 from groundwater and 2/3 comes from surface water (including artificial groundwater). The municipality waterworks reaches household, schools, hospitals, swimming pools, and many companies. In 2015, the municipalities delivered a total of over 863 million cubic meters of water.

The statistics further explains that despite the population from 1990 – 2015 increasing by around 1.3 million, household water usage has been reduced. According to statistics Sweden (2015), of about 1,750 municipalities waterworks 1,450 were groundwater plants while the remaining 170 waterworks were surface water plants. 565 million cubic meters of drinking water was used by household in 2015 which is 10 million short of household usage in 2010. The municipality groundwater plants together with the private well groundwater extractions amounted to about 48% of the total 565 million cubic meters of water consumed while the 170 surface water plants accounted for the remaining 52%. Fig. 1 shows that the county with the highest households that use water from private wells is Gothenburg County in 2015. In Sweden, public drinking water supplied by the municipalities are not fluoridated and the municipalities do not also reduce the fluoride content as long as it does not exceed 1.5 mg/l (Linuz and Mattias, 2017). According to this, it is clear that the fluoride content in public available drinking water is not only controlled by geological processes but also by the water treatment facilities. Every municipality have different standard for monitoring and controlling their public drinking water as a result of different sources and geologic characteristics. On the other hand, the monitoring and supervision of groundwater in private wells are poorly conducted and as such high fluoride concentration are a problem as they are often not treated. There is no legislation regarding the monitoring of private wells. This is a reason why we focus on the groundwater data from private wells. The fluoride content in the private wells varies greatly as shown in our data set below (Table 6 – Table 10) but the fluoride content in water treatment plant from the different municipalities are generally below 1.5 mg/l of concentration. Natural fluoride concentrations

in groundwater are dependent on the bedrock associated with the particular water source (SGU, 2013). High concentrations of fluoride have been linked to Proterozoic granites and pegmatitic igneous rocks with common fluoride-bearing minerals such as fluorite and fluorapatite (Berger T, 2016). Places like Kalmar County and the Gothenburg County are examples of areas containing high concentration of fluoride that exceed the recommended limit of 1.5 mg/l up to more 10 mg/l.

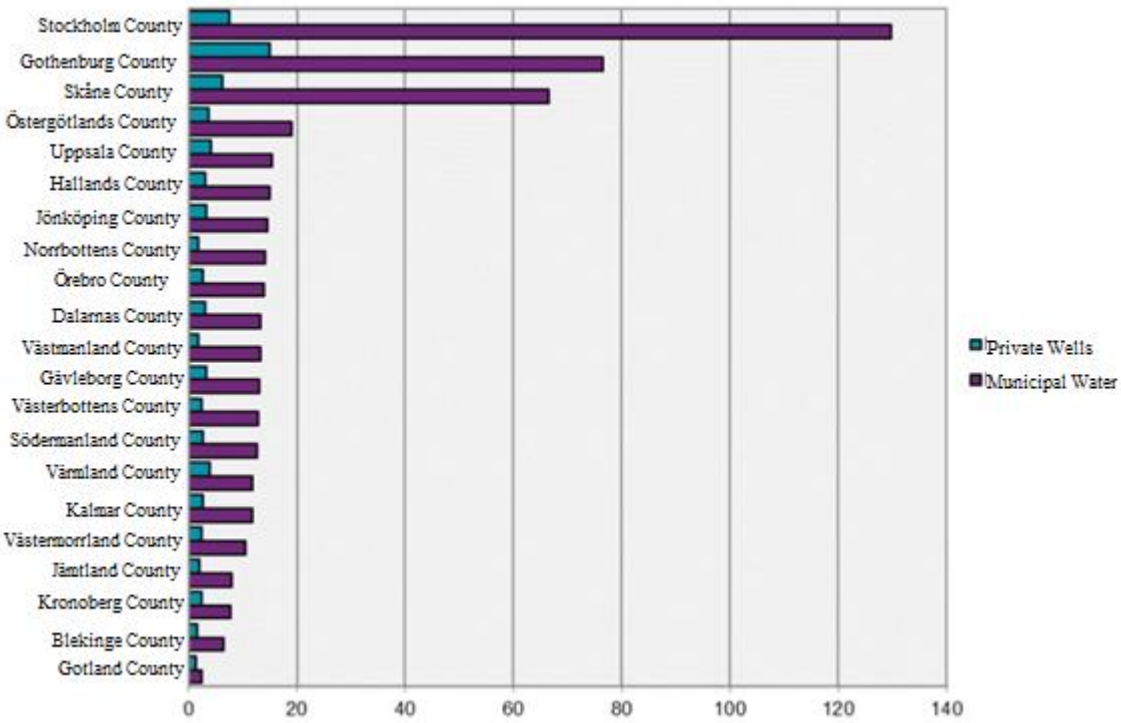

Figure 1: Household water use in 2015 by county and type of water supply, millions of cubic meters ***(****Private****).*** *Source Statistics Sweden*

1. Objectives and specific aims

The main objective of this study is to understand what controls the presence of high fluoride concentration in the groundwater in the Gothenburg area. To address this objective, we defined three specific aims

a. What proportion of the sample data is directly exposed to high fluoride concentration from their private wells?

b. Identify the sources of the minerals bearing fluoride and the corresponding rock units

c. Identify the mineral(s) that controls the presence of fluoride in groundwater in the Gothenburg area through the solubility limit of fluoride bearing minerals.

2. Background

Fluorine has a high reactivity because of its high electronegativity. Fluoride can originate from two main sources in our environment: primary and secondary sources. The primary sources of fluoride concentration in groundwater are geogenic sources, more specifically the dissolution of minerals that contain fluorine (Frencken, 1992; Berger et al, 2016). The secondary sources of fluoride are linked to pollution from industrial and agricultural activities such as the use of phosphatic fertilizers or burning of coal.

Primary sources

Primary sources are the dominant factors that are responsible for the concentration of fluoride in groundwater. The primary sources of fluoride are linked to the type of rocks/minerals that the groundwater flow through.

- **Fluorine bearing minerals**

There are about 150 fluorine bearing minerals which are classified into various categories as shown in Tab. 2 with some examples (Frencken, 1992). Of all this groups of minerals, the mineral fluorite is at present mined for economic benefits (USGS, 2017) and apatite is mined for use in phosphorous fertilizers.

There are several regions around the world that show elevated fluoride concentration in the groundwater because of the dissolution of fluorine-bearing minerals (Brunt et al., 2004). India is one of such places with millions of people suffering from the negative impact of high fluoride concentration in their groundwater. Groundwater located in northern Europe can also show high F^- concentrations being linked to the dissolution of fluorine-bearing minerals such as fluorite (CaF_2) in volcanic, granitic, and gneissic rocks (Berger et al, 2016; WHO, 2006). Some very common fluorine bearing minerals in granites and their weight % are listed in Tab. 4.

Table 2: Fluorine bearing minerals (copied from Frencken, 1992, source: Strunz, 1974)

Group	Number of different fluoride-bearing minerals	Examples
Silicates	63	Amphiboles, micas
Halides	34	Fluorite, villiaumite
Phosphates	22	Apatite
Others	30	Aragonite

- **Fluorine in rocks**

Fluorine bearing minerals like fluorite are found in granite gneisses and pegmatite (Deshmukh and others 1995; Rama Rao 1982). The highest concentration of fluorine in granitic rocks are found in micas and amphiboles (Frencken, 1992). The mineral composition of calc-alkaline granite reveals that between 30-90% of the fluorine is found in biotite with smaller amounts in other minerals like muscovite, hornblende and quartz.

The fluorine abundance in continental crust is much higher than in oceanic crust because its salts (fluorides) are less soluble in the oceans (Budisa et al, 2014). Fluorine can occur in any of the three main types of rocks: igneous, sedimentary or metamorphic rocks. The concentration of fluorine in each of these rocks can vary greatly as shown in Tab. 3.

Table 3: Concentration ranges of fluorine in major rock groups (Source: Frencken, 1992)

Type of rocks	**Fluorine concentration**
Igneous	100 ppm (ultramafic) - >1000 ppm (alkalic)
Sedimentary	200 ppm (limestones) – 1000 ppm (shales)
Metamorphic	100 ppm (regional) - >5000 ppm (contact)

Igneous and metamorphic rocks

Fluorine concentrations occur in all geological units, principally in crystalline (igneous and metamorphic) rocks (T. Berger et al., 2012; T. Berger, 2016). Fluorine is among a large group of elements that are incompatible in igneous systems meaning they are not readily incorporated into silicate minerals that crystalize from a magmatic melt. (USGS, 2017). And as such, during differentiation they accumulate in residual magmas. As mafic silicates and calcium-feldspars crystallize during the early stages of differentiating magmatic melt, there is increase in the concentrations of fluorine and silica in the residual magma (USGS, 2017; Hildreth, 1981). The incompatible nature of the element fluorine permits the mineral fluorite (CaF_2) to be present in granites, syenites, and carbonatites, where it's presence is linked to magmatic differentiation (USGS, 2017). Fluorine is also often found associated with high siliceous granite, hydrothermal mineral deposits, and alkaline rocks (T. Berger, 2016). In granitic rocks, fluorine is concentrated in both alkaline and calc-alkaline series with alkaline series hosting much higher concentrations (USGS, 2017). Fluorite is the most common fluorine-bearing mineral (Table 4) and often controls the F^- abundance in groundwater by its solubility limit.

In metamorphic rocks, fluorine is found primarily in biotite and muscovite (USGS, 2017). The highest concentration of fluoride in metamorphic rocks are formed during contact metamorphism and they are enriched during the process of metasomatism. Regional metamorphism is usually linked to lower concentrations of fluoride in metamorphic rocks. Highest fluorine concentration are usually found in amphibolite and granulite facies rocks. Their respective mineral assemblage in mafic rocks are.

- Greenschist facies: chlorite, epidote, actinolite, albite, quartz, and in rare cases phengite or biotite, or stilpnomelane, calcite.
- Amphibolite facies: hornblende, plagioclase (oligoclase-andesine) with smaller quantities of garnets, clinopyroxene, quartz, and/or biotite.
- Granulite facies: orthopyroxene, clinopyroxene, plagioclase with small amounts of garnet, hornblende and/or biotite. Fluorine concentration here could reach 3.3 weight percent in biotite contained in pyroxene-plagioclase granulite (USGS, 2017; Bose et al, 2005)

Table 4: Common F-rich minerals with granitic materials (Information compiled mainly from Correns (1956), Kokubu (1956), Palache et al. (1957), Vlasov (1966), Deer et al. (1967) and Allmann and Koritnig (1972). Recopied from Bailey 1977)

Names	Formula	F (wt. %)	Rock type
Fluorite	CaF_2	47.81–48.8	G, P, A, Gre
Cryolite	$Na_3(AlF_6)$	53.48–54.37	G, P, A, Gre
Bastnäsite	$Ce(CO_3)F$	6.23--9.94	G, P, A, Gre
Apatite	$Ca_5(PO_4)_3(F,Cl,OH)$	1.35--3.77	G, P, Gre
Muscovite	$KAl_2(AlSi_3O_{10})(F,OH)_2$	0.02--2.95	G, P, Gre
Biotite	$K(Mg,Fe)_3(AlSi_3O_{10})(F,OH)_2$	0.08--3.5	G, P, A
Hornblende	$(Ca,Na)_{2-3}(Mg,Fe,Al)_5(Al,Si)_8O_{22}(OH,F)_2$	0.01--2.9	G
Sphene	$CaTiSiO_5$	0.28--1.36	G, P, A
Topaz	$Al_2(SiO_4)(F,OH)$	13.01--20.43	G, P, A, Gre

Note: G = Granite; P = Granite pegmatite; A = Albitized riebeckite granite; Gre = Greisen

Sedimentary rocks

The most abundant halogen found in sedimentary rocks is fluorine. In phosphorites, the greatest syngenetic accumulation of fluorine occurs due to the substitution of the hydroxyl ion in apatite yielding fluorapatite. Fluoride rich minerals such as fluorite are present in carbonate sedimentary rocks in small concentrations while micas and illites are present in clastic sedimentary rocks in much higher amounts (Frencken, 1992). Other sedimentary rocks that contain high fluorine are limestone, shales, and dolomites.

Secondary sources

These sources do not affect the fluoride concentration in groundwater as strong as the geological processes. According to Ermakov (2004) the possible sources of anthropogenic sources of fluoride include: mining and processing of phosphorites, apatites, and fluorite, the production of cement, bricks, steel, aluminum and other metals as well as the combustion of coal and the production and use of fertilizers. Furthermore, the use of fluorine-bearing pesticides, and drugs as well as plastics and refrigerants.

Other factors that contribute to the occurrence of fluoride in groundwater

The factors affecting the concentration of fluoride in groundwater are dependent on the following characteristics

- Climatic conditions that the area is subjected to plays a very important role in assessing the fluoride concentration of the area. Arid climatic regions are more susceptible to contain higher concentrations of fluoride in groundwater due to its slow movement and therefore longer interaction with the rocks. High fluoride concentrations in these regions are also due to evapotranspiration. On the other hand, fluoride concentration is low in humid tropical regions where there is high rainfall which dilutes the groundwater (Brunt et al, 2004)
- Residence time: The longer (slow movement in the aquifer) that the groundwater takes to pass through a rock containing fluoride rich minerals with high potential to leach from the rock, the higher the concentration of fluoride in the groundwater. These are often associated with groundwater that located in deep aquifer systems. Shallow groundwater systems usually contain low fluoride concentrations (Madhnure et al, 2007)

3. Solubility, saturation, equilibrium constant and ionic activities

The following sections discusses the concept of mineral saturation based on the textbook by Appelo and Postma (2005) which is important to identify the mineral(s) that control the maximum F- concentration in groundwater.

3.1.Equilibrium constant

The saturation state of a solution can be quantitatively evaluated using the equilibrium constant for a specific mineral and the accordingly dissolved species. For a given reaction the equilibrium constant is defined as the ratio of the product of the concentrations of the product of the reaction to the concentrations of the product of the reactant of the reaction. These concentrations are raised to the power of their stoichiometric coefficients.

To describe the equilibrium of species in water with respect to the law of mass action of the type.

$$aA + bB \leftrightarrow cC + dD \qquad \text{..... Eq.1}$$

is given by; Equilibrium constant $K = \frac{[C]^c[D]^d}{[A]^a[B]^b}$

where the quantities in the brackets are the activities or effective concentrations.

In the following, we will explain the equilibrium constant (K) based on the dissolution-precipitation reaction of fluorite. The dissolution-precipitation reaction for fluorite is given as follows,

$$CaF_{2(s)} \leftrightarrow Ca^{2+}_{(aq)} + 2F^{-}_{(aq)} \qquad \text{…….. Eq.2}$$

the equilibrium constant is written as,

$$K_{fluorite} = [Ca^{2+}]\,[F^{-}]^2 = 10^{-10.57} \qquad \text{……. Eq.3}$$

The value $10^{-10.57}$ is constant at equilibrium and when it not at equilibrium it changes with changing physicochemical conditions. The concentration of a pure solid, $[CaF_{2(s)}]$ is equal to 1 and as such is not included in the formula. In this regard for the dissolution-precipitation reactions, the equilibrium constant is equal to the solubility product. The solubility product is the product of the ionic concentration in aqueous solution raised to its stoichiometric at equilibrium, i.e.

For the general dissolution equilibrium of the type

$$A_aB_{b(s)} \leftrightarrow aA_{(aq)} + bB_{(aq)} \qquad \text{…… Eq.4}$$

the solubility product, $K_{sp} = [A]^a[B]^b$

and sing Eq.4, we get the following

$$K_{fluorite} = [Ca^{2+}]\,[F^{-}]^2 = K_{sp} \qquad \text{……. Eq.5}$$

3.2.Activity

In expressing the law of mass action in a chemical reaction, we use the activity of the ions to be able to measure the actual concentrations of each species. The activity of a chemical species is a measure of the effective concentrations of the species. For aqueous solutes, the activity of the ions is related to molal concentration as follows:

$$[i] = \gamma_i \,.\, m_i \,/\, m_i^0 \equiv \gamma_i \,.\, m_i \qquad \text{…… Eq.6}$$

Where:

$[i]$: the activity of ion i

γ_i: the activity coefficient

m_i: molality (mol/kg H_2O)

$1/ m_i^0$: unity for all species (m^0 is the standard state of 1 mol/kg H_2O)

Substituting the activity in equation 5 gives;

$$K_{fluorite} = \gamma_{Ca2+} m_{Ca2+} \cdot \gamma^2_{F-} m^2_{F-} = K_{sp} \qquad \text{……..Eq.7}$$

To obtain the activity coefficient, we first calculate the ionic strength, *I*. The calculations of the ionic strength are based on the Debye-Hückel theory which defines the amount of electrical charges in the solution being dependent on the amount of dissolved species. The ionic strengths is represented mathematically as:

$$I = ½ \sum (m_i / m_i^0 \cdot z_i^2) \equiv ½ \sum m_i \cdot z_i^2 \qquad \text{…….Eq.8}$$

where:

Z: charge number of ion

Debye-Hückel equation for the calculation of the activity coefficient is only valid for dilute electrolyte solutions with $I < 0.1$ and its given by the following equation

$$\log \gamma_i = (-Az_i^2\sqrt{I})/(1+Bå\sqrt{I}) \qquad \text{…….Eq.9}$$

Other equations have been proposed for calculating the activity coefficient for I > 0.1. The Davies equation (Eq. 10) is applicable for ionic strength up to 0.5 and the Truesdell and Jones equation (Eq. 11) is applicable for ionic strengths of up to 2.

$$\log \gamma_i = -Az_i^2\left(\frac{\sqrt{I}}{1+\sqrt{I}} - 0.3I\right) \qquad \text{……..Eq.10}$$

$$\log \gamma_i = [(-Az_i^2\sqrt{I})/(1+Bå\sqrt{I})] + b_iI \qquad \text{……Eq.11}$$

where:

- A and B are temperature dependent constant at 25ºC is 0.5085 and $0.3285*10^{10}$/m respectively
- å is the ionic-size parameter
- b_i is ion-specific fit parameter

Appelo and Postma (2005) illustrated the relationship that exist between the activity coefficient and the ionic strength for different ions. This is shown in Fig. 2 and the symbols were calculated based on the Debye-Hückel equation (Eq. 10) while the lines are based on the Truesdell and Jones equation (Eq. 11).

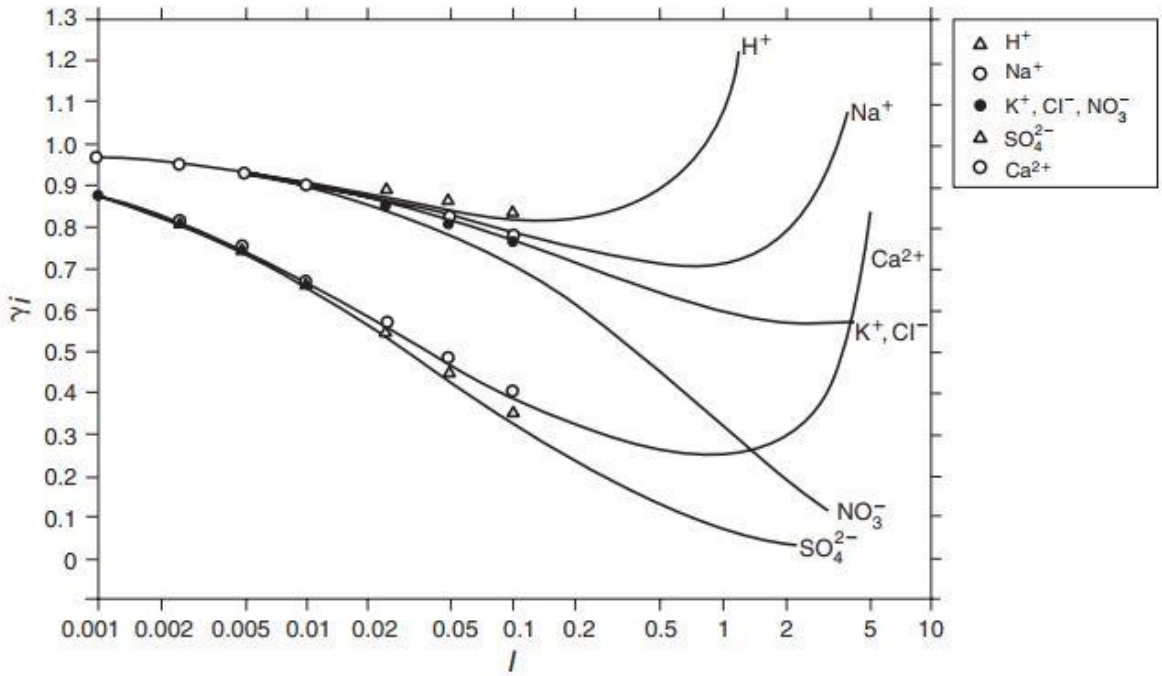

Figure 2: Activity coefficients for some common ions as a function of ionic strength. From Garrels and Christ (1965)

The lines from the Truesdell and Jones equation have similar values at low ionic strengths with the Debye-Hückel equation. Due to the action of the term $b_i * I$, higher values of ionic strength tend to increase the activity coefficient of cations.

3.3.Ion activity product (IAP)

The ion activity product is also known as the reaction quotient and is the measured amounts of reactants and products in a chemical reaction at any given time. The IAP helps in indicating which direction the reaction is proceeding. The difference between IAP and K is that, K indicates a reaction at equilibrium while IAP is not at equilibrium and represents the measured concentrations in a solution.

Considering the equation:

$$CaF_{2(s)} \leftrightarrow Ca^{2+}_{(aq)} + 2F^{-}_{(aq)} \qquad \text{……..……Eq.12}$$

The equilibrium constant of the equation in terms of activities at equilibrium conditions

$$K_{fluorite} = (\gamma_{Ca2+}\, m_{Ca2+})equil \cdot (\gamma^2_{F-} m^2_{F-})equil \qquad \text{.....Eq.13}$$

However, the dissolution - precipitation reaction of fluorite might not always be at equilibrium. The IAP is written the same way as the equilibrium constant but with the actual (measured) activities.

$$IAP = (\gamma_{Ca2+}\, m_{Ca2+})_{measured} \cdot (\gamma^2_{F-} m^2_{F-})_{measured} \qquad \text{.....Eq.14}$$

There are three main comparisons between IAP and K that exist.

- If IAP = K, then the reaction is at equilibrium. This means that the reaction doesn't shift neither to the left nor the right. No more products or reactants are formed at this point.
- If IAP > K, there exists more product than would be at equilibrium. There is precipitation and the reaction shifts to the left in favour of the reactants.
- If IAP < K, the reaction favours the products. There are more reactants than they would be at equilibrium and the system shifts the reaction to the right. There is dissolution

3.4.Solubility and saturation

Solutions are mixtures of two or more substances and occurs in a physical process rather than a chemical one. One of the substances is the solvent and the other(s) is the solute. Therefore, solubility is defined as the quantity of a solute capable of dissolving in a solvent (Brown and Lemay, 2022). The solubility limit is then defined as the limit where no more solute can be added to the solvent without precipitating a mineral at specific temperature and pressure (Brown and Lemay, 2022). Precipitation is the forming of any solid particles in the solution. In the case of the mineral fluorite, both Ca^{2+} and F^- control the solubility limit of fluorite since fluorite is composed of calcium and fluorine (CaF_2).

Saturation has three states that will be in the focus here: unsaturated, saturated, and supersaturation solution. Taking the example of Ca^{2+} and F^-, if the concentrations of both Ca^{2+} and F^- in groundwater are small such that fluorite becomes dissolved by the water molecules, the solution is termed "unsaturated" with respect to the mineral fluorite. However, if Ca^{2+} and F^- dissolution continues, the solution reaches the solubility limit of fluorite at which point the solution is saturated (in equilibrium) with respect to the mineral fluorite. At this point of saturation, the solvent has dissolved the highest possible amount of the solute and if more solute

is present, the rate of the forward reaction (dissolution) equals the rate of the backward reaction (precipitation). Any further addition of either Ca^{2+} or F^- to a saturated solution will lead then to a "oversaturation" of the solution and to the precipitation of the mineral fluorite. *(The reference for this section was taken from Brown and Lemay's Libre textbook, 2022)*

3.5. Saturation index (SI)

In the example of Ca^{2+} and F^-, the saturation index here is a useful tool to determine whether the groundwater is saturated, undersaturated, or supersaturated with respect to the mineral fluorite. The mathematical expression is shown in Eq. 15. The same is used by the PHREEQC (see Methods section for further explanation) software to calculate the SI.

$$SI = \log\left[\frac{IAP}{K_{sp}}\right] \quad \text{.....Eq.15}$$

The answer obtained from this calculation can either be negative, positive, or zero. All these signifies different states of saturation of the groundwater. In this regard, saturation will be derived as follows.

- $SI = 0$ $IAP = K_{sp}$ $\rightarrow$ Saturated (zero value, in equilibrium)
- $SI < 0$ $IAP < K_{sp}$ $\rightarrow$ Undersaturation (negative value, reaction moves from left to right, dissolution)
- $SI > 0$ $IAP > K_{sp}$ $\rightarrow$ Supersaturation (positive value, reaction moves from right to left, precipitation)

II. Study Area

The study area is located in Southeastern Sweden along the west coast of Gothenburg County as shown in Fig. 3. This chapter will focus on the geologic history responsible for the emplacement mechanism of the present rock units in the study area and a detailed description of the different rock units together with their mineralogical composition. Below is a brief summary of the formation of the different geologic units in Southwestern Sweden with focus in the Idefjorden Terrane. The geology of this part of Sweden extends into the South of Norway.

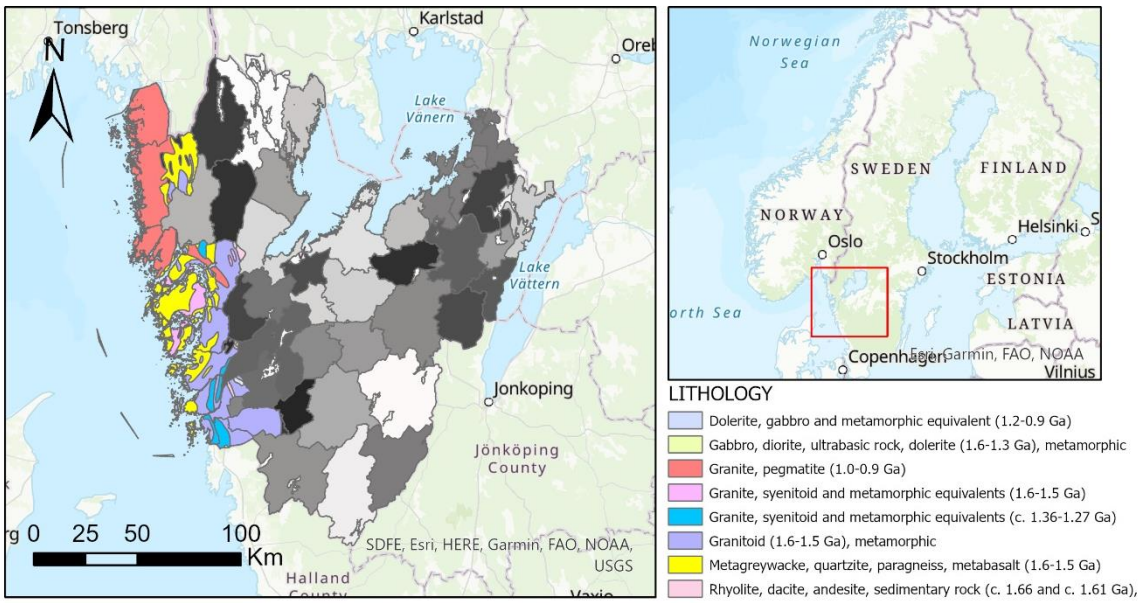

Figure 3: Map of Gothenburg County. The colored sections of the map shows the location of the different municipalities were the studies was carried out

General geological setting of the area

Geologically, the Gothenburg area consists of Pre-Cambrian bedrock that consist generally of a N-S orientated lithologic units with two main orogenic events: the Gothian and the Sveconorwegian Orogeny (L. Persson et al, 2003). The surface and valleys are covered by glacio-fluvial deposits and clays respectively. The oldest rocks found here are the supracrustal gneisses which are sometimes veined and migmatized. Other gneissic rocks include grey-red to red gneisses of granitic to tonalitic composition, greywackes and granodioritic gneisses. The Gothenburg area is found in the Idefjorden Terrane, which is west of the Mylonite zone that separates it from theso-called Eastern Segment (Figure 4).

Sveconorwegian Orogen

The Sveconorwegian orogen covers a large portion of Southwest Sweden and South Norway (Bingen et al, 2020). The Sveconorwegian Province, on the other hand is the area which was affected by that orogeny (coloured portion in Fig. 4). Bingen. et al (2020) proposed a continental collision scenario model for the formation of the Mesoproterozoic to Neoproterozoic Sveconorwegian orogeny. According to Bingen et al (2020) the Sveconorwegian orogeny occurred during the formation of the supercontinent Rodinia at the end of the Mesoproterozoic Era. The formation of the Rodinia complex was due to continental plates collision between Laurentia, Baltica, and Amazon (Bingen et al, 2020). During the Rodinia assemblage, there was a "large, hot, long-duration continental collision" event as proposed by Bingen et al (2020) that occurred between Eastern European craton (Proto Baltica) and another plate Laurentia (Greenland) which led to the formation of the Sveconorwegian orogen. The Sveconorwegian orogeny is affiliated with (and a continuation of) the Greenville orogeny along North America's eastern margin (Bingen et al, 2020). The continental lithosphere was formed between Paleoproterozoic to Mesoproterozoic and then reworked between the Mesoproterozoic to Neoproterozoic during the Sveconorwegian orogen (Bingen et al, 2020). The Sveconorwegian orogen is made up of five lithotectonic units (as shown in Fig. 4). These units stretching from East (Southern Sweden) to West (Southern Norway) are Eastern Segment, the Idefjorden terrane (which are both found in southwest Sweden), Kongsberg, Bamble, and Telemarkia lithotectonic units (these other three are found in Norway). To the east, a 700km long Sveconorwegian front separates the Sveconorwegian orogen from the Svecokarelian orogen (Foreland of the Sveconorwegian orogen). There exist major shear zones which have different geologically description in the Sveconorwegian orogen that separate the lithotectonic units.

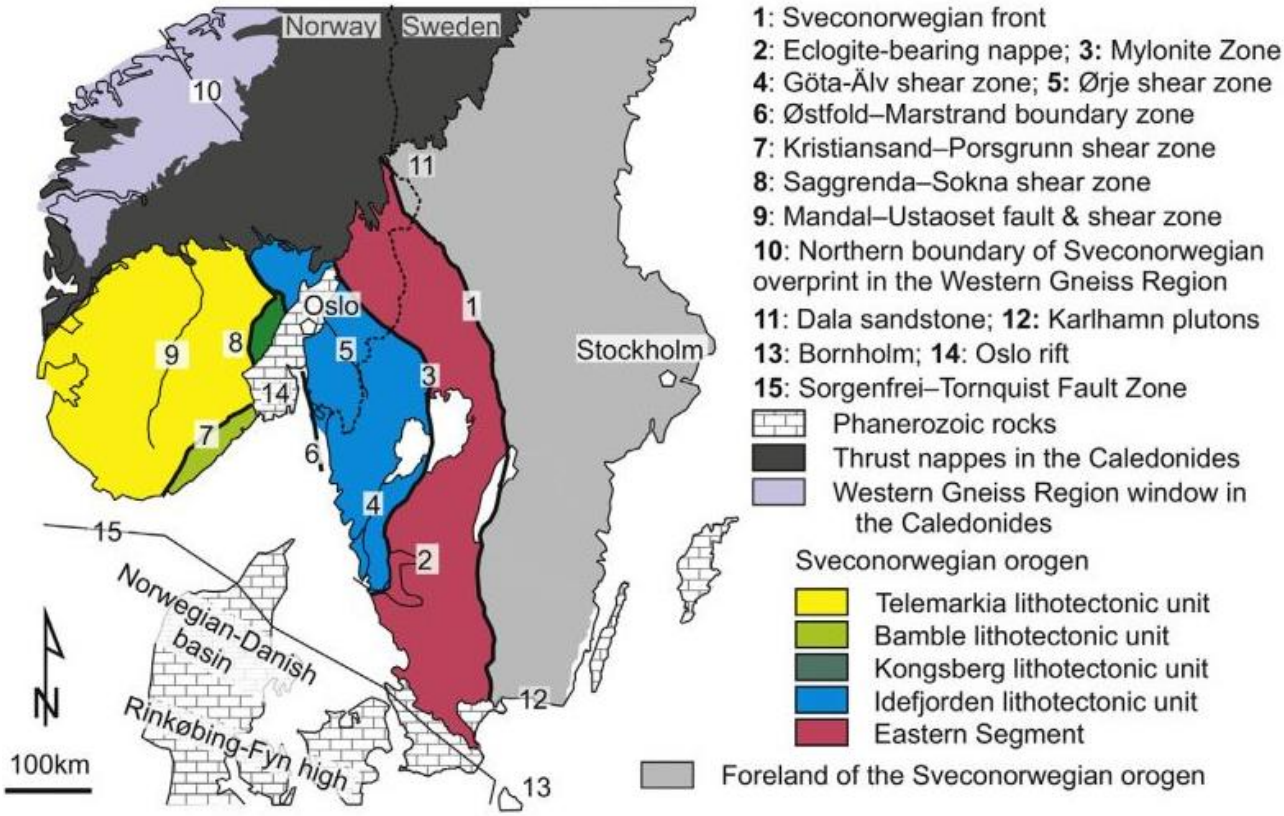

Figure 4: Sketch map of the Sveconorwegian Orogen, with nomenclature of Lithotectonic units and main shear and fault zones. (Copied from Bingen et al, 2020)

A. Idefjorden Terrane

a. Gothian and pre-Sveconorwegian evolution

The study area (Västra Götaland county) is geologically located in the Idefjorden Terrane (Fig. 3). The Idefjorden lithotectonic unit is found west of the Eastern Segment and it separated from the Eastern Segment by a west dipping Mylonite zone that is 450km long shown in Fig. 5 (Åhäll and Connelly, 2008; Bingen et al, 2020). This unit is about 140km wide and consist of rocks of plutonic and volcanic origin that were formed during the Gothian accretionary orogeny which also contain meta-sedimentary rocks, granitoids and gneisses (B. Bingen et al, 2020; A. Petersson et al, 2015).

In the Idefjorden Terrane, there exist three formations which are younger as you move from east towards to west (Åhäll and Connelly, 2008; Brewer et al, 1998; Bingen et al, 2020). These three units are

i. 1.66 - 1.64 Ga metavolcanic Horred Complex.

ii. 1.63 - 1.59 Ga metavolcanic and metasedimentary Åmål complex combined with the Göteborg granite suit.

iii. The 1.59 - 1.52 Ga metasedimentary and metavolcanic Stora Le-Marstrand complex together with the 1.58 - 1.52 Ga plutonic Hisingen Suite.

The melts formed during this evolution were described by Bingen et al (2021) as having "low to medium K calc-alkaline geochemical compositions with supra-chondritic Hf and Nd isotope signature". This evidence indicated that the magmatism was derived from a continental and oceanic volcanic arc. The 1.6 - 1.52 Ga rocks were crosscut by this magmatic bodies listed by Bingen et al (2021):

i. N-S trending Orust tholeiitic dolerite dyke

ii. Bimodal Kungsbacka suite

iii. Dals group

b. Sveconorwegian Orogeny

The structural strain of deformation during the Sveconorwegian orogeny in the Idefjorden is characterized by a N-S to NW-SE orientation. The Idefjorden terrane also consist of several shear zones, the most relevant are the Göta Älv Shear zone and the Mylonite zone (Bergström et al, 2020; Wahlgren et al, 2016; Bingen et al, 2020). The mylonite zone (almost 700km long) separates the Idefjorden terrane from the Eastern Segment and stretches uninterruptedly for about 450km. It is composed of a mylonitic fabric of a vast range of greenschist - upper amphibolite facies. The Mylonite zone is a sinistral transpressional thrust zone (Bergström et al, 2020) that places the Idefjorden Terrane on top the Eastern Segment (Stephens et al, 1996; Viola and Henderson, 2010; Viola et al, 2011). The Idefjorden terrane exhibits metamorphic facies ranging from greenschist - amphibolite - granulite facies metamorphism (Bingen et al, 2020).

B. Eastern Segment

The Eastern Segment is older than the Idefjorden Terrane. The Eastern Segment is a North-South trending belt composed primarily of granitic to quartz-monzonitic orthogneiss (Berthelsen, 1980; Möller and Anderson, 2018; Stephens and Wahlgren, 2020a; Bingen et al, 2020) and the age range between 1.8 - 1.64 Ga (Andersson et al, 2008; Bingen et al, 2008).

The rocks in the Eastern segment show both records of Hallandian age (between 1.47 and 1.38 Ga) and Sveconorwegian age metamorphic event (Christoffel et al. 1999; Johansson et al. 2001; Andersson et al. 2002; Söderlund et al. 2002). The rocks in this unit show evidence of high-pressure conditions which were formed during granulite and eclogite facies metamorphism. The Eastern segment is divided into three parts: the frontal wedge (greenschist to amphibolite facies metamorphism), the transitional section (amphibolite metamorphism), and the lower section (most metamorphosed, high-pressure granulite – amphibolite facies metamorphism). As shown in Fig. 4, it is bounded by the Sveconorwegian Frontal Deformation Zone to the east and the Mylonite Shear zone to the west.

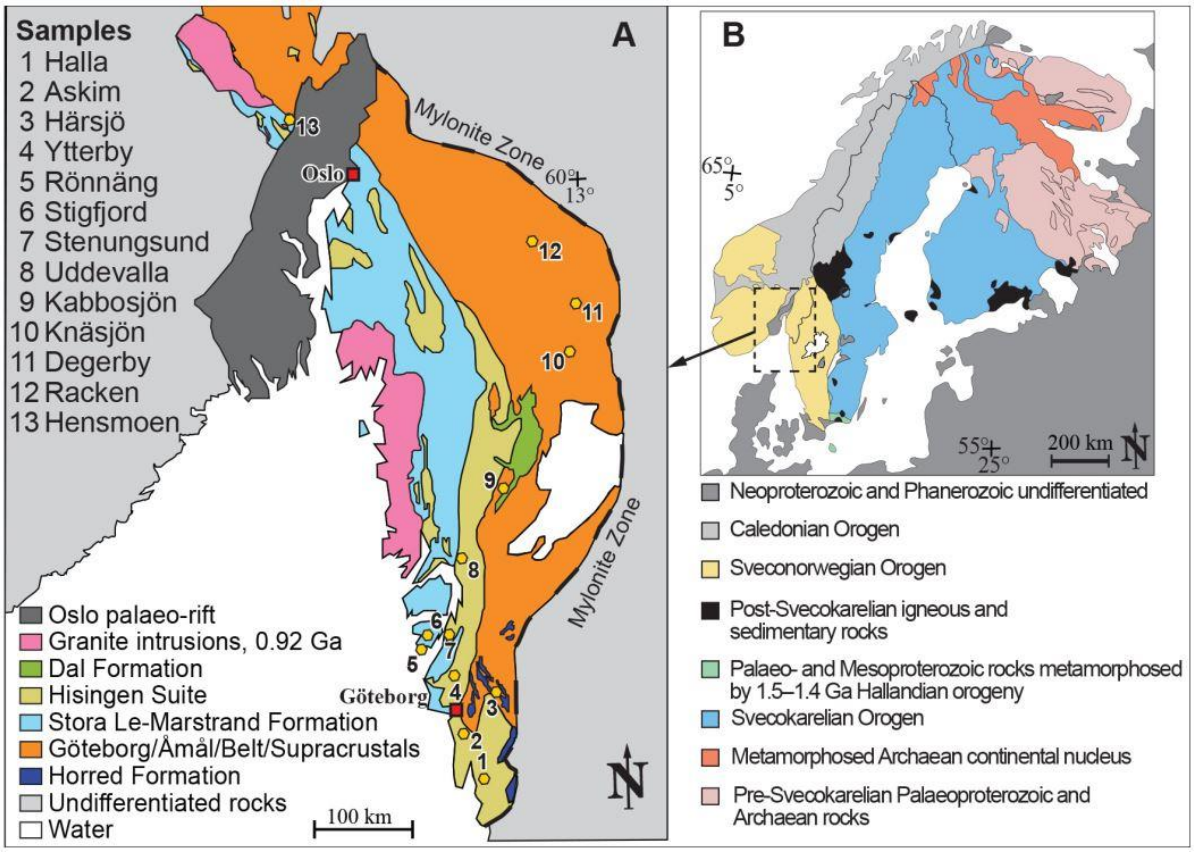

Figure 5: Idefjorden Terrane redrawn after Åhäll and Connelly (2008), with sample locations. (b) Sketch map of Fennoscandia modified from Stephens et al. (2009).

The main rock units in the Idefjorden Terrane are: the Horred formation, the Göteborg-Åmal belt, the Stora Le-Marstrand Formation, the Hisingen Suite, the Kungsbacka Bimodal Suite (KBS), and the Bohus granite. All these units are composed of different rock types each having different mineralogic composition (Tab. 5). The rocks have igneous, sedimentary, and

metamorphic origins. A look at the different rock types within each rock unit together with their respective mineralogy is discussed below with focus on the possible fluoride bearing minerals.

i. Granite Intrusions (Bohus granite)

Various mafic and felsic magma bodies intruded the coastal area of Sweden crosscutting the regional rocks that were metamorphosed under amphibolite facies conditions (Bingen et al, 2020). The Bohus granite with principal composition of biotite - muscovite intruded around 920 Ma as large tabular bodies (Bengin, et al, 2020; Eliasson et al, 2003; Schöberg, 1991). The emplacement of the Bohus granite is a post-kinematic Sveconorwegian event (Eliasson et al, 2003). The magma that formed the Bohus granite crystalised and formed biotite monzogranites with secondary muscovite. Pegmatitic-aplitic facies stabilize biotite and muscovite in the late stages of the magma. In the northern parts of the granite, there occur xenoliths of amphibolite facies of paragneiss and orthogneiss origins (Eliasson et al, 2003). During the chloritization of the biotite, there occur small amounts of epidote, pumpellyite, microcline ± albite, muscovite, rutile, titanite, fluorite, quartz, and allanite

ii. The Horred formation

This is the oldest (1.65-1.64Ma) rock unit in the Idefjorden terrane and is found in the southern part of the Idefjorden terrane (Fig. 5). The Horred formation consists of gneisses and metavolcanic rocks of dacite composition, with some basalt and rhyolite. These volcanic rocks consisted of sheets of discontinuous mafic and felsic rocks. Both dacite and rhyolite contain hornblende and biotite, among others. These minerals contain fluorine (Tab. 5) and can act as a potential source for fluoride in the groundwater of this unit.

iii. Rocks from the Göteborg - Åmal belt

They are found in the eastern part of the Idefjorden terrane and cover an extensive area. The Åmål formation located around Vänern is supracrustal consisting of metavolcanic and metasedimentary rocks. These rocks were first formed between greenschist to amphibolite facies metamorphism and then they were later regionally deformed. The vast portion of this belt is composed of plutonic (intrusive) rocks called the Göteborg/Kallebäck suite. Together

they are called the Göteborg -Åmål Belt (GAB) by Åhäll and Connelly (2008) as shown in Fig. 5. So, during the Sveconorwegian orogeny occurred the second heterogenous metamorphic after the Gothian orogeny had taken place. With the exceptions of the final stages of the Hisingen suite, all the Gothian-related rocks have undergone metamorphic alteration twice, but it is generally regarded that the Sveconorwegian orogen imprinted the widespread greenschist-amphibolite facies through most of the Idefjorden. The volcanic rocks in the Åmål formation are generally made up of intercalated feldspars and quartz porphyric rhyolites and dacites with arkosic sandstones. The fluoride-bearing minerals in greenschist facies are muscovite and biotite and that of amphibolite facies are hornblende, muscovite, amphibole, and biotite (Tab. 5). Most of the rocks are gneiss and include granitic intrusions of dacite and rhyolitic composition intercalated with pelitic and arkosic sandstones.

iv. The Stora Le-Marstarnd formations

This unit is composed of metagreywacke, granitoids and metabasalts which were deposited some 1.59 Ga. The Stora Le-Marstrand formation consists of various meta-sedimentary successions (Åhåll and Connelly, 2008), of metamorphosed turbiditic psammite and greywacke which have undergone amphibolite-facies conditions (Bingen et al, 2001). Amphibolite facies rocks contain amphiboles and micas (*Table 5*) among other minerals which are fluoride-bearing minerals that could contribute to the fluoride content in the groundwater of this unit. Bingen et al (2020) analysed paragneiss in this formation.

v. The granitoids of the Hisingen suite

The 1.58 - 1.52 Ga Hisingen Suite composed of granitoid rocks which intruded both the Göteborg - Åmål belt and the Stora Le-Marstarnd formation and therefore emplaced between the two rock units (A. Petersson et al, 2015). According to A. Petersson et al (2015), this unit has a variety of rocks such as the two-mica granite, granodiorite, granitic gneiss, two-mica granodioritic gneiss and granodiorite gneiss. In this unit, fluoride-bearing minerals such as biotite and muscovite are present with small amounts of either amphiboles or hornblende (Tab. 5).

vi. The Kungsbacka Bimodal suite

Kungsbacka bimodal suite is a set of granitic intrusions that occur 1.3 Ga (Hegardt et al, 2007). This unit has two common rock types according to the SGU report of 2006; the RA granite (which refer to the Göta granites and the Kärra granites) and the Askim granite. The

intrusion depicts a N-S trending belt from the Trollhättan in the north through the Göta Älv shear zone passing through the centre of Kungälv and Göteborg to Kungsbacka. The metamorphic data indicate that the Göta and the Kärra granites show a higher degree of metamorphism than the Askim granite. The Askim granite shows the presence of hornblende and biotite among others which are fluoride-bearing minerals, and the RA granites has also been identified in the SGU report of having elevated fluorine due to the presence of the mineral fluorite (Tab. 5). The major minerals found in the Göta granites consist of quartz, plagioclase, K-felspars, hornblende and biotite (Austin Hegardt et al, 2007). The mineral composition of the Kärra granite is similar to the Göta granite but with more K-feldspars and has abundant fluorine with fluorite occurring as an accessory mineral. In addition, the Kärra granite is radioactive and shows high levels of Th and U.

Table 5: Common fluoride-bearing minerals in the main units of the Idefjorden Terrane

Mineral	**Chemical composition**	**Geological Unit**					
		Horred formation	Göteborg-Åmal Belt	Stora Le-Marstrand formation	Hisingen suite	Kungsbacka Biomodal Suite	Bohus Granite
Fluorite (fluorspar)	CaF_2	**X**	**X**	**X**	**X**	**X**	**X**
Biotite	$K(Mg,Fe)_3(AlSi_3O_{10})(F,OH)_2$	**X**	**X**	**X**	**X**	**X**	**X**
Muscovite	$KAl_2(AlSi_3O_{10})(F,OH)_2$		**X**	**X**	**X**		**X**
Hornblende	$(Ca,Na)_{2-3}(Mg,Fe,Al)_5(Al,Si)_8O_{22}(OH,F)_2$	**X**	**X**	**X**	**X**	**X**	
Apatite	$Ca_5(PO_4)_3(F,Cl,OH)$		**X**	**X**	**X**		

III. Data and Methods

An outline of the different methods that were used to collect and evaluate the used data in this thesis is presented below.

1. Data

a) Geochemical groundwater analysis

The analysis on the groundwater samples collected from private wells around Västra Götaland County was conducted by 6 different laboratories: Alcontrol AB, Karlstrona Kommun laboratorium, Eurofins Environment Testing Sweden AB, Eurofins Pagasuslab AB, Miljönämndens i Trellborg Lab, and Analycen AB. The samples were collected from approximately 7148 wells along the West Coast of Västra Götaland County over a period of 9 years from 2007 to 2016. The results of the analysis contained about 35 different parameters including temperature, pH, and major cations and anions. To identify sources of fluoride in groundwater in the Gothenburg region and to determine how the fluoride in the groundwater concentrations are controlled through the solubility limit of fluoride-bearing minerals, some of the data was not used because they lacked measurements for calcium and/or fluoride which are important for the interpretation of the results.

b) Geographical data

The geographic data used consisted of both vector and raster layer maps of rocky types and other properties. Access to these maps was provided by several sources as outlined in detail below:

- Vector shape files of the fault structures, rock distribution, soil depth, groundwater capacity, reservoir flowrate and municipalities boundaries were downloaded from Lantmäteriet and Geological Survey of Sweden (SGU) via The Swedish University of Agricultural Sciences (SLU). These maps contained information about the different lithotectonic units and their ages, the hydrogeological maps, and the maps of Västra Götaland county with all its various municipalities. The underlying map is from ©OpenStreetMap.
- Warehouse management systems (WMS) links of radiometry measurements (Th and U) were obtained from the Geological Survey of Sweden (SGU),

2. Methods

a) Excel and GIS Software

After preparing and filtering of the geochemical data obtained from the lab, they were converted to comma separated values format (*.csv*). This *.csv* format will transform the data from the excel sheet to points representing sample locations in ArcGIS Pro and QGIS software. The maps from Lantmäteriet and SGU are in shapefiles formats that QGIS and ArcGIS Pro can read and alter them. The coordinate reference system used in this project is SWEREF 99 TM (Swedish Reference Frame 1999 Transverse Mercator). Both the comma separated values and the shapefiles were superimposed and processed together as discussed in chapter IV.

b) Sample location

The samples that were used for this study in the Idefjorden terrane were located only in 12 out of the 48 municipalitiesin the Gothenburg County: Göteborg, Härryda, Kungälv, Lysekil, Mölndal, Orust, Sotenäs, Stenungsund, Stömstad, Tanum, Tjörn, and Uddelvalla Municipalities. Fig. 6 below shows the map of sampled fluoride concentration located along the coastline of the Gothenburg County. The samples are unevenly sampled across each of the major rock units in the Idefjorden terrane. Some units like the Bohus granite have a full representative of samples in the whole area while other rock units like the Stora-LeMarstrand and the Goteborg and Åmal belt have only a small portion of their total surface area that was sampled.

c) PHREEQC

The speciation of fluoride in the groundwater of the Gothenburg area and saturation indices of the different fluoride-bearing minerals was assessed using PHREEQC (version 3) by using the groundwater sample analysis from the private wells as input data.

PHREEQC stands for **PH RE**dox **EQ**uilibrium in **C** programming language. The version 3 of PHREEQC is written in C and C++ programming language. This program works on the basis of equilibrating the chemistry of aqueous solutions as they interact with minerals, gases, solid solutions, exchangers, and sorption surfaces (Parkhurst and Appelo, 2013).

According to Parkhurst and Appelo 2013, the PHREEQC considers several different aqueous models, which are

- two ion-association aqueous models (the Lawrence Livermore National Laboratory model and WATEQ4F),

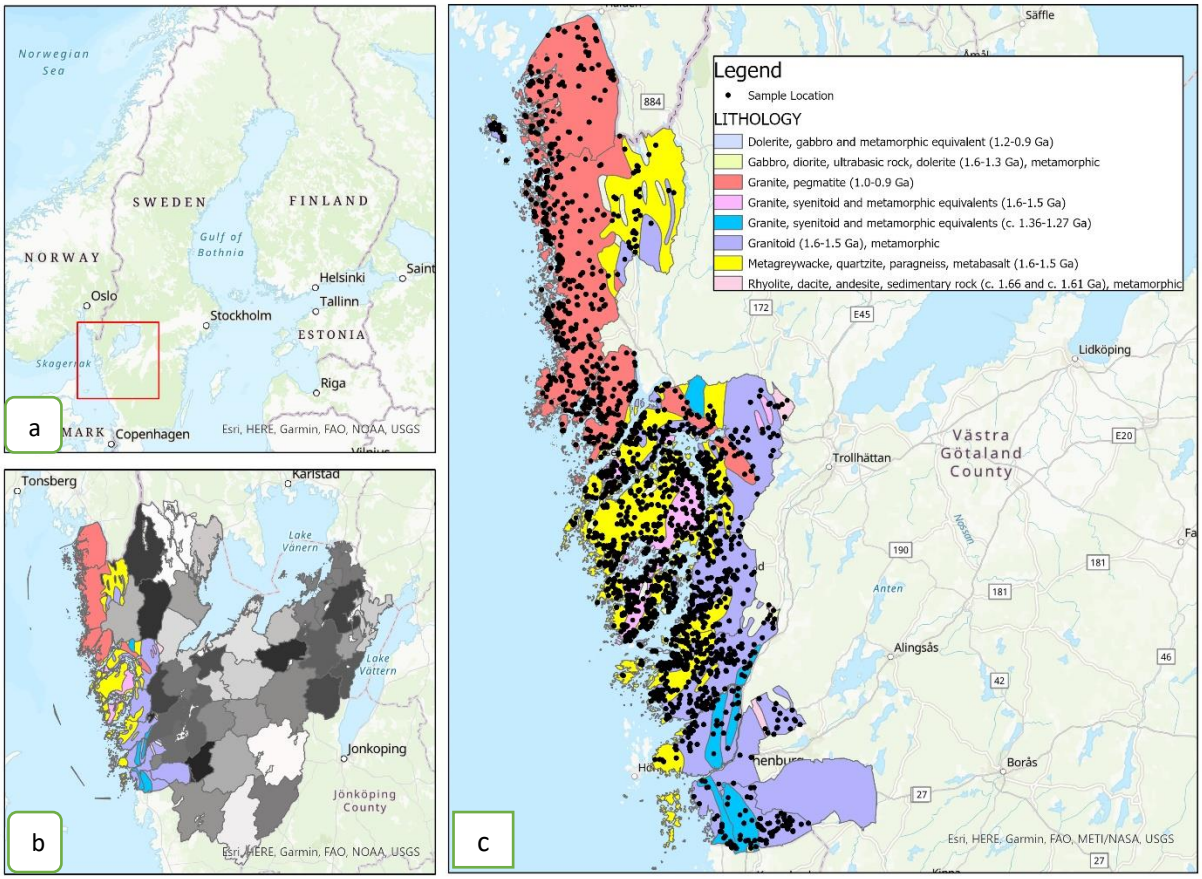

Figure 6: a) Map of Sweden b) Gothenburg County c) Study Area with sample locations (source: Lantmäteriet)

- a Pitzer specific-ion-interaction aqueous model, and
- the SIT (Specific ion Interaction Theory) aqueous model

PHREEQC has the capabilities to perform the following:

1. speciation and saturation-index calculations.
2. batch-reaction and one-dimensional (1D) transport calculations with reversible and irreversible reactions,
3. inverse modelling,

For the purpose of this studies, the focus will be on the speciation and saturation-index calculations in the PHREEQC program. The program is executed with the help of NotePad++ to calculate the different species and their saturation indices. The code (with the file format *Fluorite.phr*) for the calculation of the speciation has already been written and is only open in

NotePad++. The database file (PHREEQC.DAT) used contained all the various mineral phases and their formula together with their solution species which are used in the calculation of the saturation indices. The calculation will yield all the various possible mineral phases and their saturation indices.

IV. Results and discussion

The results of all the data collected and the applied methods for analysing these data will be described here and divided into two subsections.

- The first section will present the results obtained on the concentration of fluoride measured in groundwater obtained from the private wells within each rock unit found in the Idefjorden Terrane. These results together with the regional geology on the minerals found in each rock unit, will be used in trying to understand the possible source(s) responsible for the high fluoride in the groundwater of these rock units. Also, the relationship that exist between the high fluoride concentration regions and radioactive isotopes of uranium and thorium is evaluated.
- The second subsection will focus on two parts: firstly, the geochemical modelling using PHREEQC to determine the mineral(s) that controls the maximum F^- concentration in the groundwater and then then the solubility limit diagram of the mineral(s) mentioned above.

1. Fluoride groundwater concentrations in different geologic units.

The distribution of the different rock types together with the fluoride groundwater concentration data from the private wells were compiled in GIS software as shown in Fig. 7, 8, and 9 and some statistical analysis was carried to understand how the different group of concentrations varied within each rock unit. Below is a detail description of the different group of fluoride concentrations contain within each overlayed rock unit. Some of the rock units do not have a good representative sample collection and thus it is not possible to give a correct generalized conclusion on the whole rock unit.

- **The Horred Formation**:

The Horred formation is a small rock unit with respect to the area it covers compared to the other rock units. Only 13 samples were collected from this rock unit in this study shown in Fig. 7 and 8. Based on the lab test on the samples collected, the statistics of the fluoride concentration is shown on Tab. 6 is as follows.

- 53.85% of low fluoride concentration between 0.1 mg/l to 0.5 mg/l and
- 30.76% of the samples measured high fluoride concentration between 2 mg/l to 16 mg/l.
- With the remaining 15.38 % of the samples being with the accepted levels of fluoride concentration.

Despite it being a small rock unit compared to the others, the samples collected here cannot give a true approximation of the fluoride concentration in this rock unit. Earlier in the text, it was mentioned that the highest concentration of fluorine in metamorphic rock is found in micas specifically in biotite which is found in the gneissic rocks in this unit and therefore expect that there be more samples with fluoride concentrations. The location of houses in this unit shows that there are many more private houses that data was not collected from.

Table 6: Statistics of fluoride concentration from private wells in the Horred formation.

Fluoride concentration	*Number of sampled wells*	%
0 - 0.5 mg/l	7	53.85
0.5 - 1.5 mg/l	2	15.38
1.5 – 3 mg/l	2	15.38
3 – 16 mg/l	2	15.38

– **The Kungsbacka bimodal suite**:

The samples that were identified on the map as belonging to the Kungsbacka bimodal suite were 57. Fig. 7. 8, and 9 all show that this unit contains concentrations of fluoride varying from very low to very high values. The statistics of fluoride concentration listed in Tab. 7 in this rock unit are as follows.

- 47.73% of the samples measured had fluoride concentrations below 0.5 mg/l whereas 19.3% had concentrations above the 1.5mg/l.
- 33.33% of the samples measured fluoride concentration fall within the acceptable limit of 0.5 – 1.5 mg/l.
- 8 samples here recorded concentrations above 3 mg/l and up to 16 mg/l. This confirms the high fluorine content in this unit which was reported by Hegardt et al, 2007. These high concentrations of fluoride have a strong relation with the radioactive granites i.e., the Göta and the Kärra granites found in this rock unit. The Kärra granites have been documented by Hegardt et al, 2007 of being rich in fluorite in pegmatite dykes.

Looking at Fig. 11 and 12 below, these high fluoride concentrations coincide direction with regions of high radioactive readings of both Uranium and Thorium.

Table 7: Statistics of fluoride concentration from private wells in the Kungsbacka Bimodal suite

Fluoride concentration	*Number of sampled wells*	%
0 - 0.5 mg/l	27	47.37
0.5 - 1.5 mg/l	19	33.33
1.5 - 3 mg/l	3	5.26
3 - 16 mg/l	8	14.04

– **The Göteborg-Åmal belt** and the Hisingen granites

The rocks from the Hisingen suite do not have a separate vector file data and as such its boundary limits are mixed with the shapefile data from the Stora LeMarstrand formation and the GAB. Most of the Hisingen Suite is joined with the GAB. Closer examination of the sampling data showed that most of the data collection was toward the granite of the Hisingen Suite. These rock units both cover a very large area and though the 641 samples collected here seems a lot, it represents less than a quarter of the total area of this massive rock unit.

The statistics of the results are represented on Tab. 8 below.

- 54% of the groundwater samples had fluoride concentrations from 0 to 0.5 mg/l and 34% range from 0.5 to 1.5 mg/l. From Tab. 1 above, more than 50% of the people using private wells in this rock unit are likely to have dental caries from prolong exposure compared to the 11% exposure to fluorosis.
- It shows here that only about 11% of the samples had high fluoride groundwater concentrations. From the maps shown in Fig 7 and 8, these sampled wells were located closer to the west of the boundary limit corresponding to samples collected from the Hisingen Suite. As shown below, the granites in the Hisingen Suite content high fluoride in their groundwater and some of this fluoride might have leached out to its surrounding and ended up in the Göteborg granites and the. The maps in Fig. 7 and 8 show that the fluoride concentration within the Göteborg granite (most easterly rocks)

far from its boundaries with Hisingen Suite are primarily below 1.5 mg/l. The presence of fluoride bearing minerals like biotite, muscovite, amphibole, and hornblende in this unit are likely responsible for the detected fluoride concentrations.

Table 8: Statistics of fluoride concentration from private wells in the Göteborg – Åmal belt and the Hisingen Suite.

Fluoride concentration	*Number of sampled wells*	%
0 - 0.5 mg/l	351	54.76
0.5 - 1.5 mg/l	219	34.17
1.5 - 3 mg/l	48	7.49
3 - 16 mg/l	23	3.59

– **The Stora Le-Marstrand rock unit**:

The shapefile downloaded contained part of the rock shapefile from the Hisingen Suite and the Stora Le-Marstrand rock units. In the Stora Le-Marstrand section, the private wells were sampled much closer to the west as shown in Fig. 7. This rock unit is made up of primarily metamorphosed sedimentary rocks and some granites. 1249 samples were collected in the Stora Le-Marstrand and part form the Hisingen Suite. Majority of the samples in Tab. 9 recorded fluoride concentrations in the groundwater between 0 - 0.5 mg/l which amounted to about 50% of the all the sampled data. 35% of the samples recorded concentrations of fluoride within the acceptable limits of 0.5 to 1.5 mg/l. The remaining 15% recorded values of high fluoride concentration above 1.5 mg/l. This high fluoride concentration is also associated with of the Hisingen Suite.

Identification of the rocks making up the Hisingen Suite was done visually. The granitoid in the Hisingen Suite shown in Fig. 7, 8, and 9was estimated to have between 300 to 350 sampled private wells. There were quite fewer samples for the lower range of 0.0 mg/l below detection limit (b.d.l.) to 1.5 mg/l fluoride concentration. The granitoid showed more than 50% of the samples with high levels of fluoride concentration between 1.5 mg/l to 4 mg/l. About 30 samples (between 8.6% to 15%) range between 4 mg/l to up 9 mg/l.

Table 9: Statistics of fluoride concentration from private wells in the Stora Le-Marstrand

Fluoride concentration	*Number of sampled wells*	%
0 - 0.5 mg/l	614	49.16
0.5 - 1.5 mg/l	442	35.39
1.5 - 3 mg/l	131	10.49
3 - 16 mg/l	62	4.96

– **The Bohus Granite**:

This unit had approximately 556 sampled points with a maximum fluoride groundwater concentration of 8.9 mg/l. Unlike the other rock units that were not sampled properly or the sampling didn't cover their whole extent, this unit had a representative sample collection that covered all its edges from north to south. In Tab. 10, 31% of samples recorded high fluoride concentrations above 1.5 mg/l in the groundwater. One can comfortably say that the rocks here have the highest fluoride concentration in their groundwater that is distributed over the whole area. The presence of abundant micas, hornblende, and the appearance of fluorite likely accounts for these high values and contribute to the measured groundwater fluoride concentrations in general. These minerals are rich in fluorine and can be affected by weathering that can cause them to be leached and enter the groundwater systems.

Table 10: Statistics of fluoride concentration from private wells in the Bohus granite

Fluoride concentration	*Number of sampled wells*	%
0 - 0.5 mg/l	176	31.65
0.5 - 1.5 mg/l	208	37.41
1.5 - 3 mg/l	110	19.78
3 - 16 mg/l	62	11.15

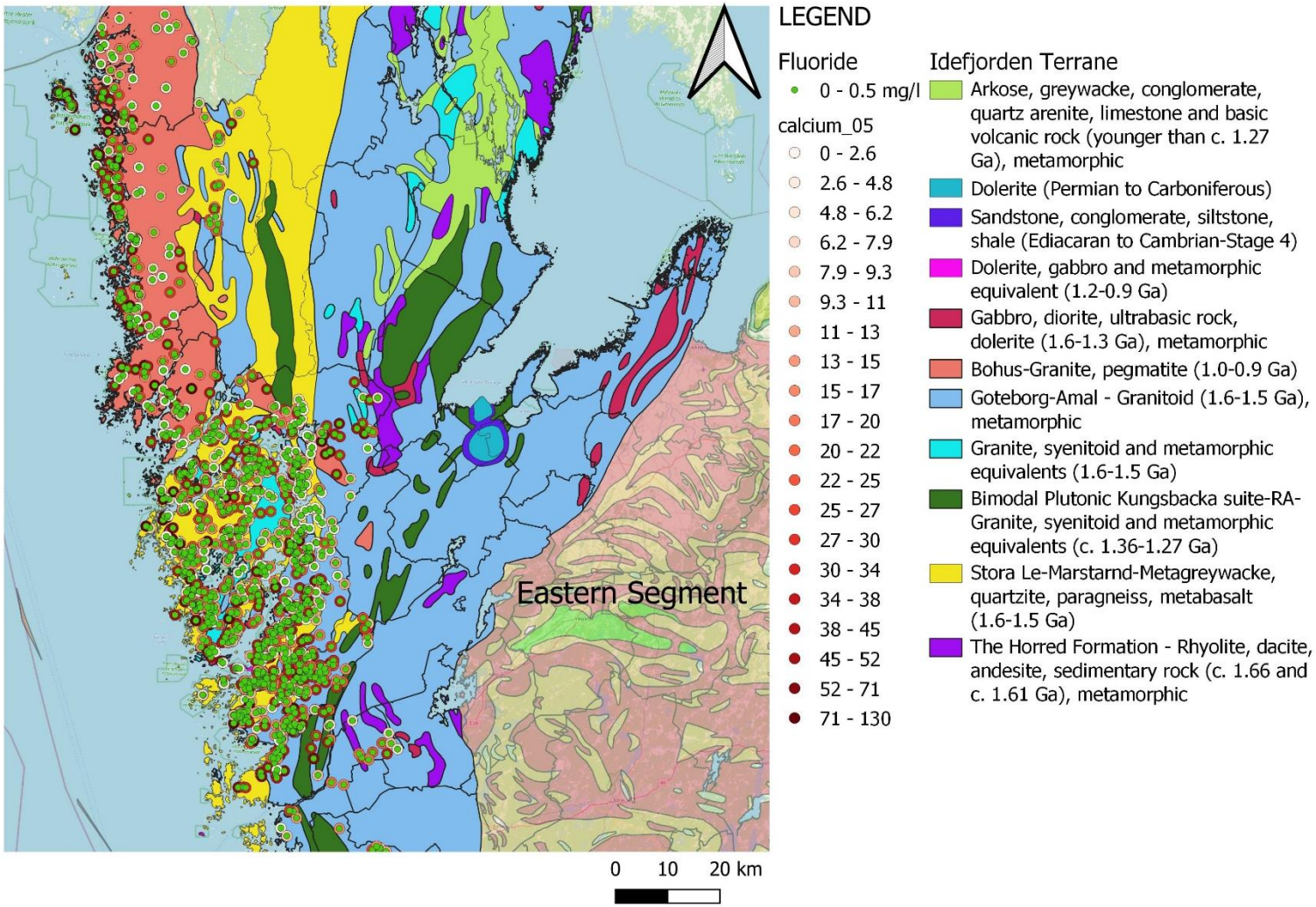

Figure 7: 0.5-1.5 mg/l Fluoride concentration and 0-510 mg/l Calcium concentrations in the Idefjorden Terrane

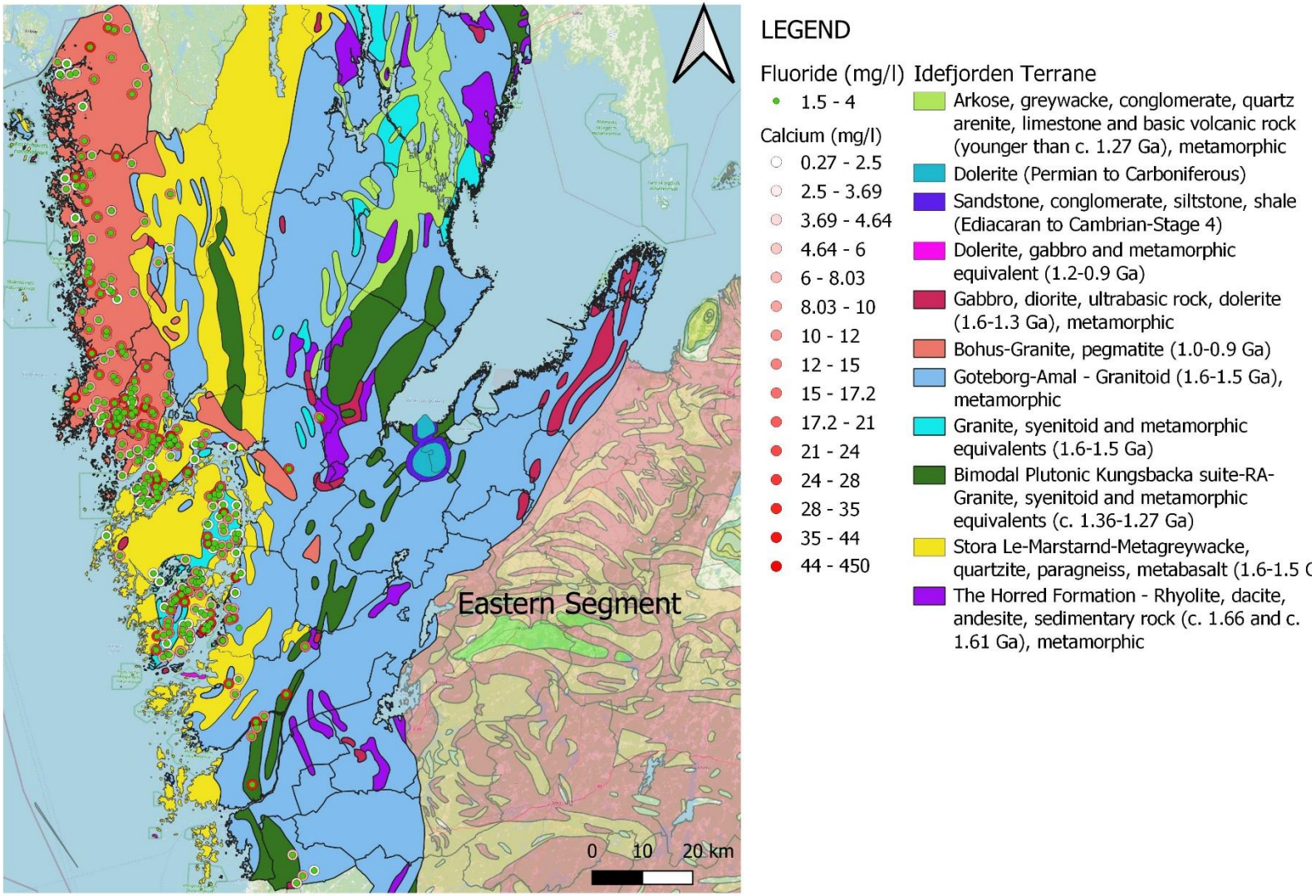

Figure 8: 1.5 – 4 mg/l Fluoride concentration and 0-450 mg/l Calcium concentrations in the Idefjorden Terrane

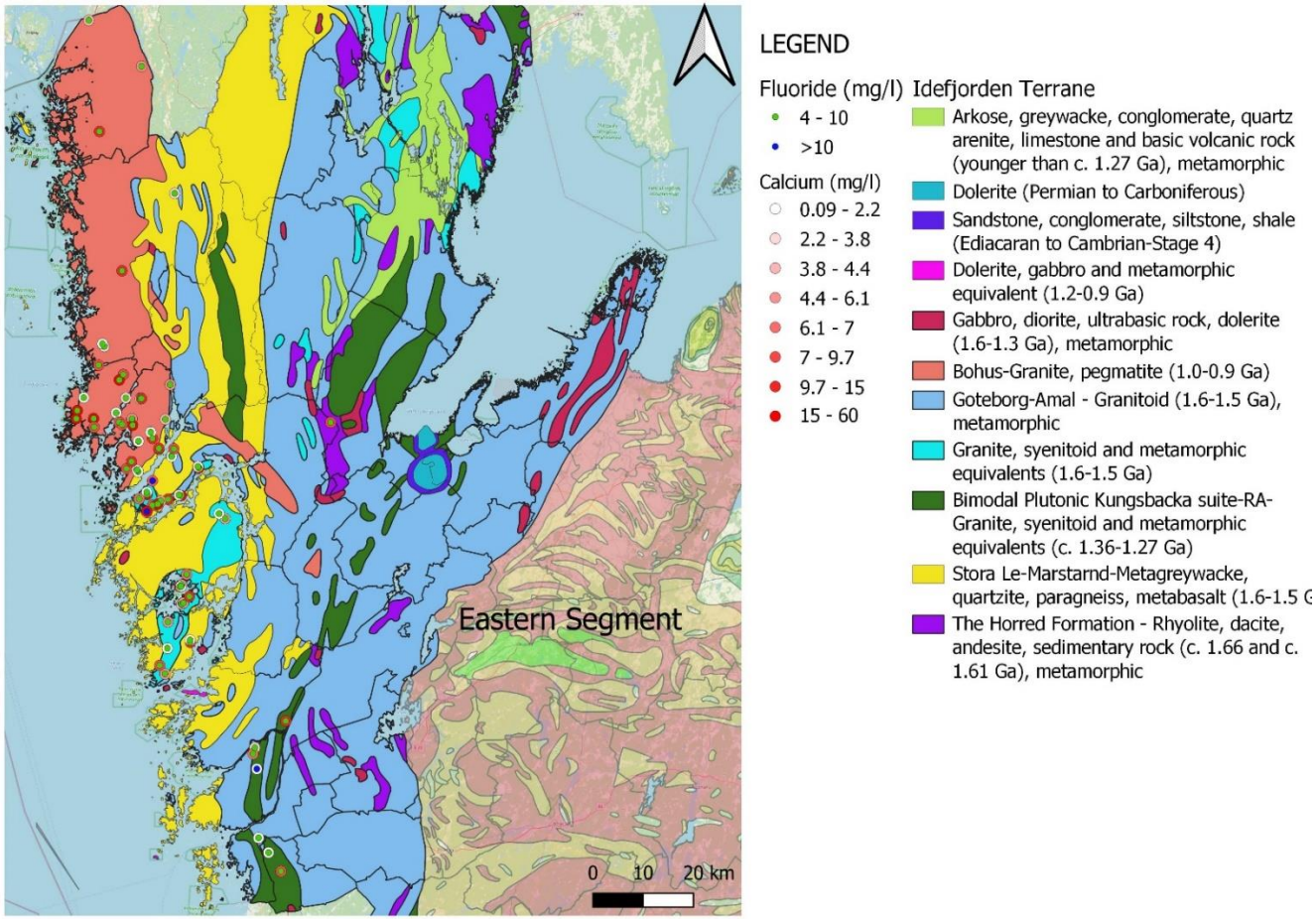

Figure 9: 4 - 16 mg/l Fluoride concentration and 0 - 60 mg/l Calcium concentrations in the Idefjorden Terrane

- **Relationship of fluorite with Thorium and Uranium**

Since the 1960 SGU has carried out airborne gamma-ray surveys in order to measure the natural gamma-ray emitters from the ground. This is being done by measuring the natural occurring concentrations of radioactive isotopes in the uppermost part of the bedrock and soil (SGU). Fig. 10 below shows the map of uranium distribution over the southwest of Sweden. The sample points of high fluoride concentration (>1.5 mg/l) are directly overlayed in the areas of high uranium measurements (3 ppm to more than 5 ppm). The uranium measurements are very high and spread throughout the Bohus granite. Also, we see from the map in Fig. 10 that there is a high uranium measurement associated with high fluoride concentrations in the Kungsbacka Bimodal Suite which is in line with the work of Hegardt et al (2007). We can also see the high uranium activities in the granites of the Hisingen Suite linked to high fluoride measurements. This can be due to the "*high stability of U(IV)-F and U(VI)O_2-F complexes*", (Xing et al, 2019). Uranium and thorium exist in the lattice of the mineral fluorite because of the similarity of the ionic radius with calcium (Ca^{2+}: 0.99 Å, U^{4+}: 0.97 Å, Th^{4+}: 1.02 Å). This only happens when the concentrations of uranium and thorium are in small amounts. In larger quantities, minerals rich in Uranium and thorium will crystalize in fractures.

In Fig. 11, one can see a similar pattern of the distribution of thorium with that of uranium in Fig. 10. The concentration of thorium is much high and spread across the same rock units as that of uranium map in Fig 11. Thorium measurements 6 ppm up to more than 19 ppm were associated with the measured high fluoride concentration (>1.5 mg/l) in the groundwater. High fluoride measurements in the Bohus granite, Hisingen Suite, and the Kungsbacka suite were link to these thorium measurements.

The reason for the co-occurrence of fluorite, uranium, and thorium is because of their incompatible nature and late-stage crystallization during the fractionation of magma.

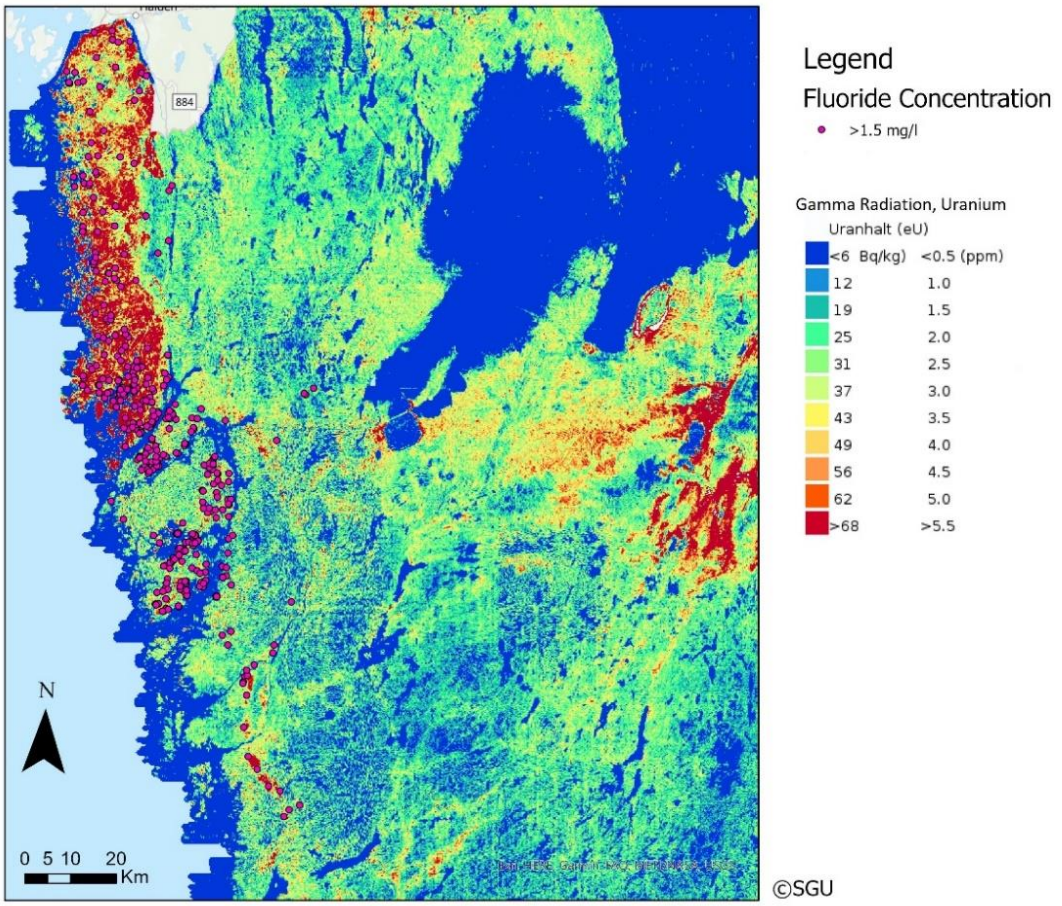

*Figure 10:*Uranium and high fluoride concentration (measurements of Uranium from 1960-2020). Source SGU

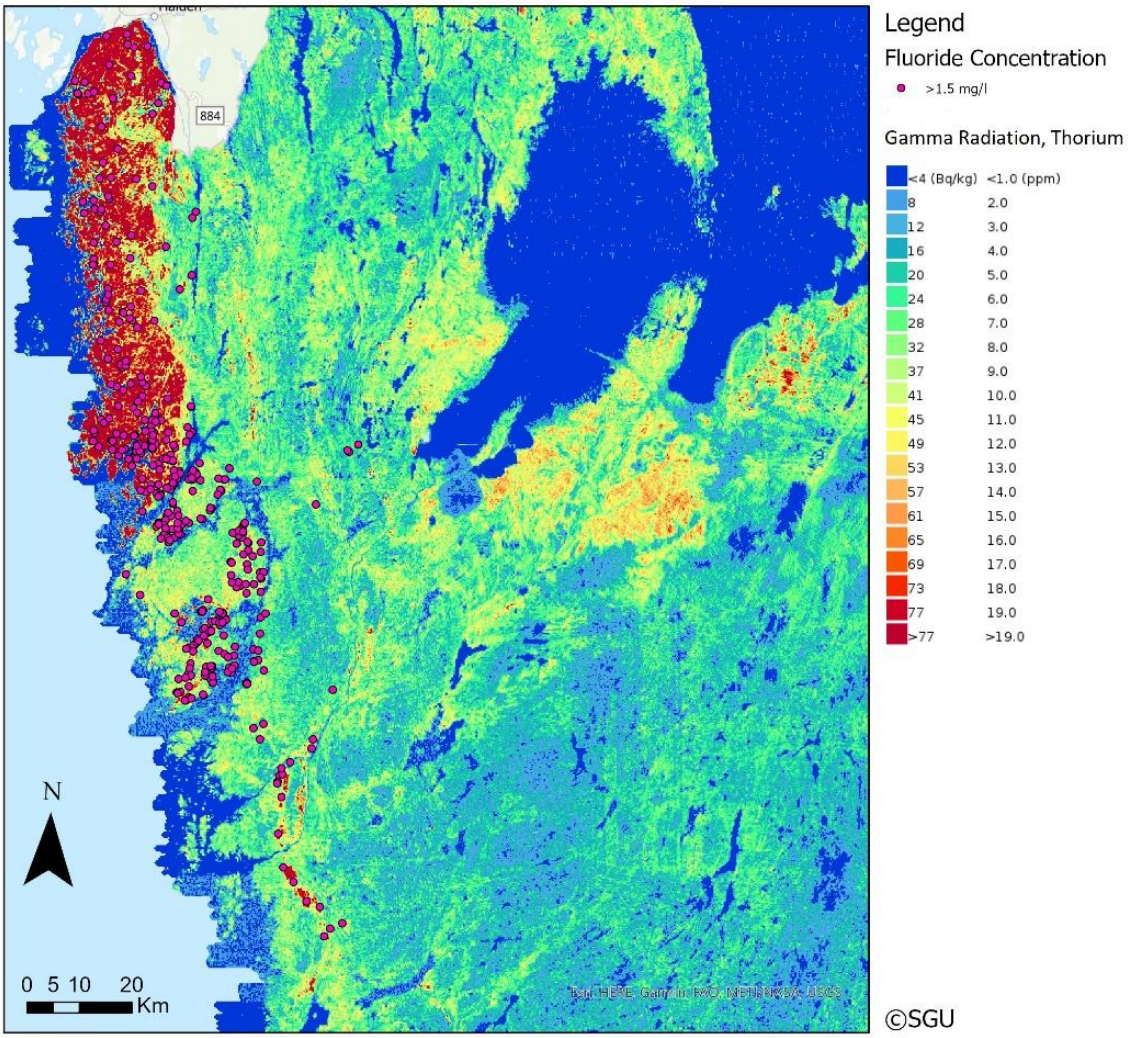

Figure 11: Thorium and high Fluoride concentration (measurements of Thorium from 1960-2020). Source SGU.

2. Which minerals controls the fluoride concentration in the groundwater in the Gothenburg area?

a. Assessing the saturation of the mineral fluorite in the different rock unit

Generally, lower fluoride concentrations were present and varied almost uniformly in all the different rock units (Fig 7). Though most of the sampling centered around the city of Gothenburg and its environs, the majority of these samples showed to be relatively more concentrated around the rock units in the Stora Le-Marstrand formation. Higher concentrations of fluoride are shown to be restricted in granitic intrusions most especially the Bohus granite in the northwest and in the Hisingen Suite (Fig. 8 & 9). The samples were collected over a period of 9 years but there was no evidence of temporal variation. Only the spatial variation in the different rock units could be easily observed.

The concentration of fluoride and calcium at each sample point was overlayed together. This is because calcium controls the concentration of fluoride and to observe the spatial variation of both substances in the different rock units. This relationship shows that the solubility of the mineral fluorite (Fig. 12) is directly proportional to the calcium concentrations. Hence, if calcium is lacking in these aqueous solutions higher fluoride concentrations are necessary until the solubility limit of the mineral fluorite is reached. On such a large data set, it is easier to the see the inverse relationship that exists between calcium and fluoride. Out of the 7148 private wells that were sampled, only 2537 had values for both calcium and fluoride which are required in for the calculations. From the statistics on Tab. 11 below, it shows that 453 (17.86%) of the 2537 sampled private wells had concentrations of fluoride that were higher than the recommended 1.5 mg/l by the WHO. Generally, most of the concentration of calcium falls below the 80 mg/l with a few values going above 100 mg/l to value of more 400 mg/l. In Fig. 7, we see that the distribution of acceptable levels of fluoride concentration (0.5 – 1.5 mg/l) measured in the groundwater is found in all the bedrocks. The level of calcium concentration was in the ranges of 0 – 80 mg/l in the acceptable fluoride concentration levels while in the high fluoride concentration shown in Fig. 7, the range between 0 – 15 mg/l.

Below, the solubility diagram of Ca^{2+} and F^{-} was plotted on a log-log graph as presented in Fig. 12 and the focus was on the mineral fluorite. This solubility diagram was plotted using the concentration of fluoride and calcium of the 2537. The solubility diagram helps to easily visualize the solubility conditions which the fluoride and calcium concentration exist in the groundwater either as undersaturated, saturated, or supersaturated. In aqueous solutions, the maximal concentration of fluoride is controlled by the solubility product of fluorite, $K_{fluorite}$

(Eq. 5). This equation is used to calculate and plot the fluorite solubility limit represented by the red line which separates samples that are undersaturated (below the red line) and supersaturated (above the red line). From the diagram in Fig. 12, it shows that increasing (moving towards the right) the concentration of the calcium will require lower concentration of fluoride to reach saturation and decreasing (moving towards the left) the concentration will require higher concentration of fluoride to reach saturation.

Table 11: Statistics of fluoride concentration from private wells along the coast of the Idefjorden Terrane.

Fluoride concentration	*Number of sampled wells*	%
0 - 0.5 mg/l	1185	46.73
0.5 - 1.5 mg/l	898	35.41
1.5 - 3 mg/l	296	11.67
3 - 16 mg/l	157	6.19

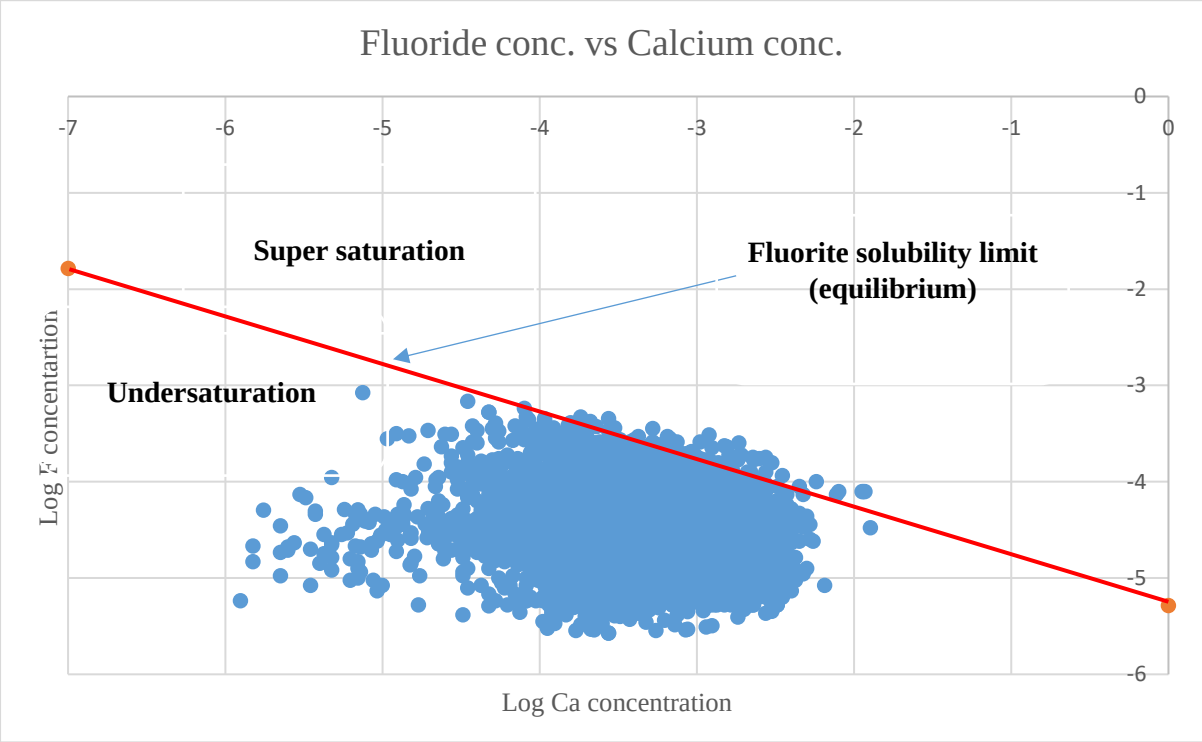

Figure 12: Solubility diagram of fluorite: Fluoride vs Calcium concentration.

b. PHREEQC Simulation

Geochemical modelling using PREEQC was used to determine the saturation index (SI) of fluorite and other fluorine-bearing minerals in the different rock units and to evaluate which fluorine-bearing minerals control the max F- groundwater concentration in Gothenburg area.

In Tab. 12, the results of the saturation indices, of fluorite are displayed for selected samples, representing each rock unit. The range of fluoride and calcium concentration varied from low to high. The results of the calculation of the SI with respect to all the anions and cations present in all 89 samples showed that only the mineral fluorite (CaF_2) was close or at saturation. This therefore indicates that only the F^- groundwater concentration is mainly solubility controlled by the mineral fluorite and not by other fluoride-bearing minerals. The SI of the samples revealed that the mineral fluorite controls the highest F- concentration through the solubility limit.

The calculated saturation indices with respect to fluorite can also be used as an indicator to tell us whether the groundwater will precipitate fluorite or dissolve it. As mentioned above in *section 1.v*, in case the value is negative dissolution might occur, whereas positive values indicate that precipitation might occur, and zero indicates chemical equilibrium. The saturation indices from the results showed that about 95% had negative calculated values. This means that fluorite is mainly dissolving in groundwater. This is supported by the solubility diagram in Fig. 12. The samples with high fluoride concentration values that were used in this calculation had negative values which were much closer to saturation than those with low fluoride concentration values. The SI of these 89 samples is plotted in Fig. 13 to show how it varies in the different rock units. The SI for samples in the Bohus granite had negative values much closer to zero with a few above zero being supersaturated with respect to fluorite. The groundwater found in both the Hisingen Suite and the Kungsbacka Bimodal Suite follow a similar pattern as almost all the SI values were negative indicating undersaturation with respect to fluorite. In the Stora Le-Marstand and the Göteborg – Åmal belt, the SI values calculated here show that the fluoride in groundwater exist almost entirely as undersaturated in groundwater as shown in Fig. 13.

The SI calculated above revealed that most of the samples were undersaturated in groundwater having a negative value. According to these results, it indicates that the mineral fluorite plays a significant role in the occurrence of fluoride in groundwater.

The results shown in Fig. 12 therefore indicates that high fluoride groundwater will occur in areas that are deficient in calcium. The results show that most of the values fall below the solubility limit of the mineral fluorite. These results are in line with the large samples of negative SI value calculated above which also indicates undersaturation. The groundwater is unsaturated with fluoride with very small fluorite that precipitate.

Table 12: Saturation indices

X_utvalda	Y_utvalda	SI Fluorite		X_utvalda	Y_utvalda	SI Fluorite		X_utvalda	Y_utvalda	SI Fluorite
298 806	6 437 730	-1.79		299 564	6 433 550	-0.35		299 156	6 478 010	-0.4
284 909	6 484 110	-1.26		285 911	6 488 510	-0.28		292 530	6 478 110	-0.05
293 000	6 479 780	-0.71		286 996	6 492 170	-0.52		292 530	6 478 110	-0.21
361 319	6 250 780	-0.21		296 258	6 475 510	-0.84		292 530	6 478 110	-0.45
281 327	6 512 490	-1.44		300 373	6 470 880	-0.71		296 622	6 466 080	-0.14
285 818	6 516 150	-0.45		293 803	6 473 760	-0.88		300 437	6 470 790	-0.59
331 073	6 354 660	-1.48		322 198	6 390 230	-0.16		302 261	6 445 570	-0.54
300 593	6 439 100	-0.66		285 012	6 476 490	-0.15		316 623	6 413 060	-0.59
301 028	6 521 900	-0.8		365 728	6 219 490	-0.75		301 878	6 463 300	-0.75
302 402	6 445 862	-0.78		365 728	6 219 490	-1.1		317 720	6 396 730	-1.5
282 876	6 497 300	-1		302 390	6 442 150	-0.37		300 133	6 484 730	-0.41
289 800	6 499 780	-1.19		304 118	6 434 700	-0.18		303 398	6 447 910	-0.33
293 749	6 467 830	0.19		295 500	6 460 110	-0.72		300 851	6 472 300	0.28
293 815	6 467 520	-0.61		295 447	6 459 900	-0.61		294 200	6 481 988	-0.45
291 505	6 459 640	-1.52		301 985	6 445 490	0.11		294 413	6 482 030	0.18
296 676	6471170	-0.99		302 261	6 445 520	-0.4		286 667	6 492 660	-0.89
299 678	6 438 660	-0.46		289 392	6 479 270	-0.87		582 979	6 356 090	-0.11
293 540	6 468 160	-1.32		317 377	6 410 120	-0.64		369 348	6 190 980	-1.32
357 719	6 220 200	-2.08		313 583	6 473 900	-2.55		319 953	6 431 090	-14.45
356 557	6 198 620	-2.19		288 258	6 543 530	-0.72		308 811	6 402 200	-1.7
363 433	6 142 990	-0.81		279 384	6 529 980	-2.03		316 690	6 403 150	-0.5
307 071	6 434 010	-0.03		305 191	6 467 890	-1.88		319 340	6 420 460	-1.59
617 516	6 334 200	-0.89		307 960	6 458 530	-2.72		320 993	6 422 000	-1.76
603 297	6 368 280	-0.4		292 036	6 449 240	-2.18		322 566	6 425 310	-2.16
323 847	6 437 550	-0.49		318 758	6 385 410	-3.17		311 715	6 403 710	-2.45
328 717	6 465 770	-1.25		286 302	6 533 860	-1.71		330 154	6 410 140	-1.67
328 532	6 469 690	-1.6		281 635	6 538 470	-2.73		322 192	6 385 100	-1.69

330 005	6 476 340	-0.36		283 933	6 555 490	-0.72		327 200	6 430 640	-0.7
327 473	6 408 360	-3.9		305 928	6 462 660	-2.54		323 161	6 421 070	-2.47
325 524	6 383 550	-4.48		297 846	6 451 230	-2.36				

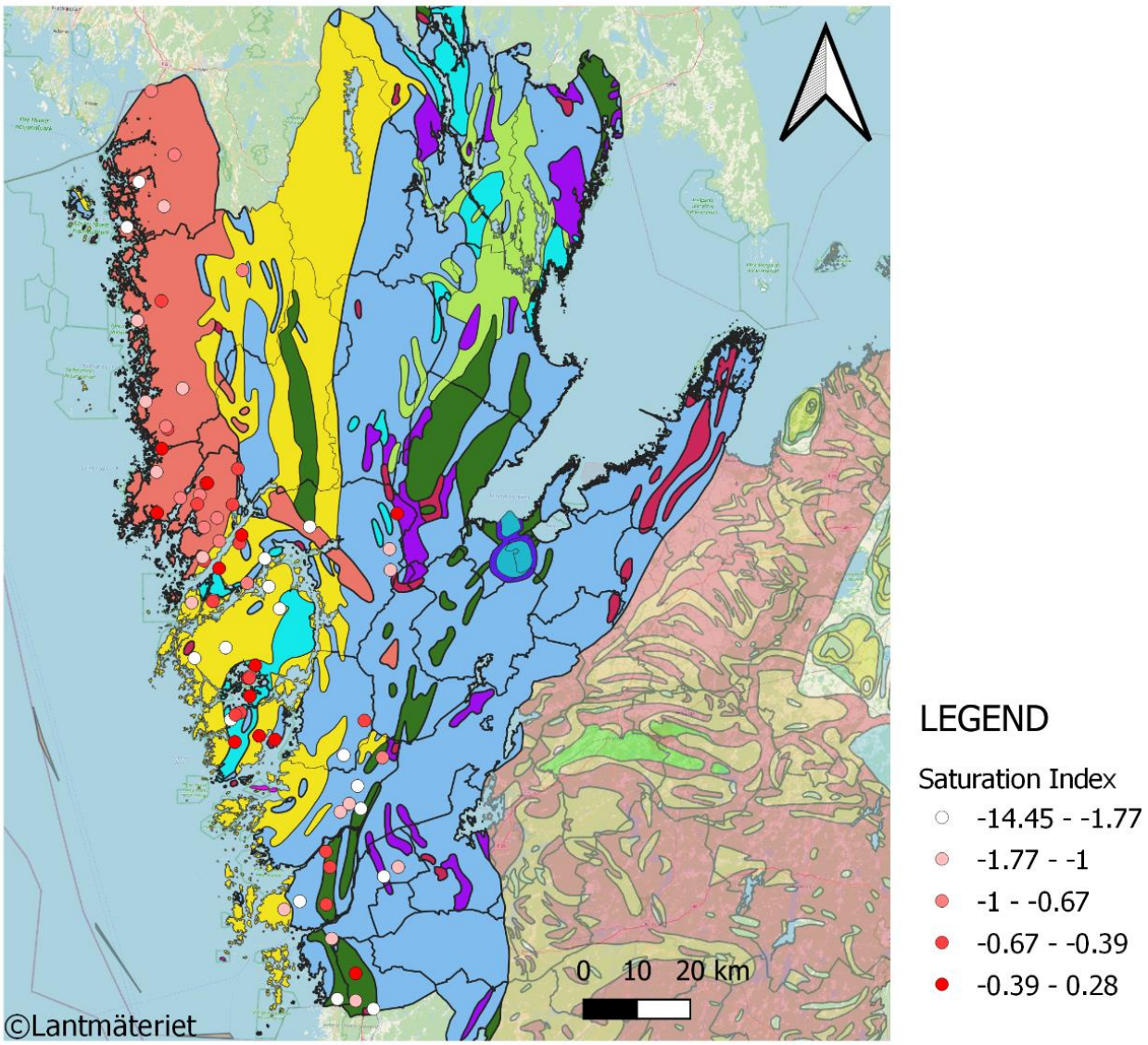

Figure 13: Saturation Indices across the Idefjorden Terrane

Conclusion

In this thesis, it has been shown that fluorite is the main mineral that controls the maximum F^- concentration in groundwater in Western Sweden through its solubility limit. It is most likely dissolved from rocks containing fluorine-rich minerals, such as fluorite, into groundwater. There are other minerals that contain minor amounts fluorine such as biotite and hornblende which also play a role in the presence of fluoride in groundwater but to a lesser extent compared to fluorite.

Based on the area within which the data was collected (within the 12 municipalities), 17.86% of household recorded concentrations of fluoride more than the recommended limit of 1.5 mg/l by the WHO and therefore risk adverse effects of high fluoride intake. The presence of high fluoride concentrations in groundwater has a strong relationship to basement rocks and in our study area more specifically to granitoids as they contain high concentrations of fluorite, biotite, muscovite, hornblende, and amphiboles. From the northwest (Bohus granites) to the southwest (Horred formation), the concentration of fluoride extends from a cluster of high fluoride concentrations to lower concentrations of fluoride. These rocks are also characterized by high radioactivity which is connected to fluorite occurring in the bedrock. The presence of fluorite enrichment in the mineralization of uranium is that it helps to remove and mobilize uranium by means of forming stable U-F complexes.

Future studies

For future studies I would recommend further analysis on the various types of the fluoride-bearing minerals to be carried out on a more local scale to have a better understanding of its spatial variation. Also, more samples be collected in the other houses found in the Idefjorden terrane so that we can have a complete picture of how minerals control the fluoride in the whole terrane.

I would also recommend further studies to be carried out to have a better understanding of the relationship that exist between the radioactive isotypes and the fluoride-bearing minerals.

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Reference

1. Appelo, C. and Postma, D. (2005) Geochemistry, Groundwater and Pollution. 2nd Edition, Balkema, Rotterdam. http://dx.doi.org/10.1201/9781439833544.

2. Andreas Petersson, Anders Scherstén, Bernard Bingen, Axel Gerdes, Martin J. Whitehouse, Mesoproterozoic continental growth: U–Pb–Hf–O zircon record in the Idefjorden Terrane, Sveconorwegian Orogen, Precambrian Research, Volume 261, 2015, Pages 75-95, ISSN 0301-9268, https://doi.org/10.1016/j.precamres.2015.02.006.

3. Edmunds, M.W., Smedley, P.L., 2013. Fluoride in Natural Waters. In: Selinus, O.E. (Ed.), Essentials of Medical Geology: Revised Edition, pp. 311-336.

4. Brunt, R., Vasak, L., Griffioen, J., 2004. Fluoride in groundwater: Probability of occurrence of excessive concentration on global scale. SP 2004-2.

5. Bingen, B., Birkeland, A., Nordgulen, Ø., Sigmond, E.M.O., 2001. Correlation of supracrustal sequences and origin of terranes in the Sveconorwegian orogen of SW Scandinavia: SIMS data on zircon in clastic metasediments. Precambrian Res. 108, 293–318

6. Hitzman, M., Valenta, R., 2005. Uranium in Iron Oxide-Copper-Gold (IOCG) systems. Economic Geology, 100: 1657-1661

7. McGloin, M.V. et al., 2016. Release of uranium from highly radiogenic zircon through metamictization: The source of orogenic uranium ores. Geology, 44(1): 15-18.

8. Parkhurst, D.L., and Appelo, C.A.J., 2013, Description of input and examples for PHREEQC version 3—A computer program for speciation, batch-reaction, one dimensional transport, and inverse geochemical calculations: U.S. Geological Survey Techniques and Methods, book 6, chap. A43, 497 p., available only at http://pubs.usgs.gov/tm/06/a43/.

9. R. Gnanavel and S. M. Mazhar Nazeeb Khan (2013), Geochemistry and role of calcium for the availability of fluoride in the groundwater of Pappireddipatti Block, Dharmapuri district, Der Chemica Sinica, 2013, 4(1):56-62

10. Sudarsan Sahu, Utpal Gogoi, N.C. Nayak (2020), Groundwater solute chemistry, hydrogeochemical processes and fluoride contamination in phreatic aquifer of Odisha, India, Geoscience Frontiers 12 (2021) 101093.

11. Saxena, V.K., Ahmed, S., 2003. Inferring the chemical parameters for the dissolution of fluoride in groundwater. Environmental Geology, 43(6): 731-736.

12. S. Ayoob & A. K. Gupta (2006), Fluoride in Drinking Water: A Review on the Status and Stress Effects, Critical Reviews in Environmental Science and Technology, 36:6, 433-487, DOI: 10.1080/10643380600678112

13. Åhäll, K.I., Connelly, J.N., 2008. Long-term convergence along SWFennoscandia: 330 m.y. of Proterozoic crustal growth. Precambrian Res. 163, 402–421

14. Tobias Berger, Frédéric A. Mathurin, Henrik Drake, Mats E. Åström (2016), Fluoride abundance and controls in fresh groundwater in Quaternary deposits and bedrock fractures in an area with fluorine-rich granitoid rocks, Science of the Total Environment 569–570 (2016) 948–960

15. Berger, T., Peltola, P., Drake, H., Åström, M., 2012. Impact of a fluorine-rich granite intrusion on levels and distribution of fluoride in a small boreal catchment. Aquat. Geochem. 18 (2), 77–94

16. UNICEF, 2018. UNICEF Policy Brief: Mitigating Arsenic in Drinking Water.

17. Viola, G., Henderson, I.H.C., Bingen, B., Hendriks, B.W.H., 2011. The Grenvillian–Sveconorwegian orogeny in Fennoscandia: back-thrusting and extensional shearing along the “Mylonite Zone”. Precambrian Res. 189, 368–388

18. WHO, 2008. Guidelines for drinking-water quality. Third Edition Incorporating the First and Second Addenda. World Health Organization, Geneva.

19. WHO, 2006, Fluoride in Drinking water.

20. WHO, 2011 Guidelines for Drinking-water Quality Fourth edition. World Health Organization, Geneva., World Health Organization.

21. SGU, 2013. Kemiarkivet (The Groundwater Chemistry Archive) © SGU, Swedish Geological Survey. Assessed 2013-03-12.

22. https://www.britannica.com/science/metamorphic-rock/Zeolite-facies#ref75144

23. https://ec.europa.eu/health/scientific_committees/opinions_layman/fluoridation/en/l-3/2.htm

24. https://sustainabledevelopment.un.org/post2015/transformingourworld/publication

25. Carrard N, Foster T, Willetts J. Groundwater as a Source of Drinking Water in Southeast Asia and the Pacific: A Multi-Country Review of Current Reliance and Resource Concerns. *Water*. 2019; 11(8):1605. https://doi.org/10.3390/w11081605
26. United Nations, *The 2030 Agenda and the Sustainable Development Goals: An opportunity for Latin America and the Caribbean* (LC/G.2681-P/Rev.3), Santiago, 2018